SYNTHESIS AND CHARACTERIZATION OF NOVEL MACROCYCLIC LIGANDS CONTAINING N, O OR S DONOR ATOMS AND THEIR COMPLEXES

ABSTRACT

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

BY

HAMIDA - TUN - NISA CHISTI

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

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ABSTRACT

The continued interest and quest in designing new macrocyclic ligands and their complexes stem mainly in view of their variety of applications. This interest was stimulated by the possibilities macrocycles offered to the creative chemist to investigate molecular recognition in new ways and therefore suggest ideas for the design and synthesis of novel complexes capable of performing useful functions. Among the macrocycles the synthesis of aza-macrocyclic compounds received considerable attention during the last few decades because of their relationship to biomimetic and catalytic systems and the applications of this type of chelating agents to biology and medicine. They have applications in modern clinical techniques such as magnetic resonance imaging, imaging with radioisotopes and radiotherapy, i.e., techniques where metal complexes with extreme kinetic and thermodynamic stability toward metal release are required. The whole thesis is divided in five different chapters.

First chapter gives a general introduction to macrocyclic complexes and the pioneering work done by eminent scientists. A systematic description of conventional methods of synthesis, the physical and chemical properties, reactivities, functionalities and

applications has been accounted on various types of macrocyclic compounds involving N, P, O, and S donor atoms. The effect of ring sizes, nature of the ligand donors, donor set, donor array, ligand conjugation, ligand substitution, number and sizes of the chelate rings, ligand flexibility and the ligand backbone to tailor specific metal ion or recognition of molecular species has been discussed. The applications of macrocyclic complexes in development of bioinorganic chemistry, therapeutic agents, medically important chemicals, synthetic ionophores etc. have also been highlighted.

Second chapter deals with the basic principles and theories of various techniques used in the characterization of the newly synthesized macrocyclic complexes viz., infrared spectroscopy, nuclear magnetic resonance spectroscopy, electron paramagnetic resonance spectroscopy, ultraviolet and visible spectroscopy, magnetic susceptibility and molar conductance measurements, elemental analyses, thermogravimetric analysis, job's method and antimicrobial activity.

Third chapter describes the synthesis and characterization of 14- and 16-membered octaazamacrocyclic complexes, Dichloro/nitrato [1,2,4,5,8,9,11,12-octaazacyclotetradecane] metal(II), $[ML^1X_2]$, (M =

Co(II), Ni(II), Cu(II) and Zn(II); X = NO_3 or Cl) and Dichloro/nitrato [1,2,4,5,8,9,10,12,13-octaazacyclohexadecane] metal(II), $[ML^2X_2]$, (M = Co(II), Ni(II), Cu(II) and Zn(II); X = NO_3 or Cl). These macrocyclic complexes were synthesized by reacting hydrazine, formaldehyde and 1,2-dibromoethane or 1,3-dibromopropane with metal ion in a 4:2:2:1 molar ratio. The low molar conductance values measured in DMSO suggest their non-electrolytic nature. The confirmation regarding the formation of macrocyclic framework in the complexes has been achieved by loss of absorption bands characteristics of NH_2 groups of the hydrazine moiety and the presence of ν(N-H) in the region 3210-3260 cm^{-1} and appearance of proton resonance peaks in the regions, 6.86-6.94, 3.08-3.19, 2.90-2.95 and 1.80-1.90 ppm assigned to (C-NH-N), (N-CH_2-C), (N-CH_2-N) and (C-CH_2-C) protons, respectively in the IR spectra of the complexes and ^1H NMR spectra of Zn(II) complexes, respectively. The magnetic susceptibility data and the band positions in the electronic spectra of Co(II), Ni(II) and Cu(II) complexes ascertained the octahedral geometry of the macrocyclic complexes. However, the EPR spectra of the Cu(II) complexes show $g_{\|} < 2.3$ which indicate that they exhibit appreciable covalent character.

The fourth chapter discusses the synthesis and characterization of hexaazamacrocyclic complexes, Dichloro/nitrato [3,5:12,14-dipyridyl

8,9:17,18-dibenzo-2,4,6,11,13,14-hexacyclooctadecane-1,6,10,15-tetraene] metal(II), [MLX_2], (M = Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or NO_3), resulted from the template condensation reaction of o-phthalaldehyde and 2,6-diaminopyridine with metal ion in a 2:2:1 molar ratio. The elemental analyses obtained compliment the proposed stoichiometry of the complexes. The IR spectra of all the complexes do not show bands corresponding to amino or carbonyl groups, instead a strong intensity band appeared around 1610 cm^{-1} assigned to the coordinated ν(C=N). The characteristic ring vibrations of the pyridine moiety and the phenyl ring vibrations appeared at their estimated positions. The bands around ~1410, 1230 and 1015 cm^{-1} indicate the presence of coordinated nitrate group in the complexes derived from metal nitrates. The ^1H NMR spectrum of [$ZnL(NO_3)_2$] shows a singlet at 8.08 ppm corresponding to the four equivalent imine protons, CH=N (4H). The spectrum shows a triplet (δ_H 8.05 ppm) and a doublet (δ_H 7.73 ppm) assigned to the *para* H_a and *meta* pyridyl H_b protons, respectively. A doublet and a triplet observed at δ 6.89 ppm and δ 7.26 ppm corresponds to H_1 and H_2 protons of phenyl moiety, respectively. However, the ^1H NMR spectrum of [$ZnL(NO_3)_2$] does not show any bands assignable to the uncondensed NH_2 and CO moieties of 2,6- diaminopyridine and *o*-phthalaldehyde supporting the formation of macrocyclic framework.

The EPR spectra of the Cu(II) macrocyclic complexes show a broad signal in which $g_{\parallel} > g_{\perp}$ suggesting that $d_{x^2-y^2}$ is the ground state and the G values of 2.00 and 1.91 for $[CuL(NO_3)_2]$ and $[CuLCl_2]$ complexes suggest the exchange interaction between copper centers. The electronic spectral and magnetic moment data of Co(II) and Ni(II) complexes indicate a perfect octahedral geometry around the metal ion while Cu(II) complexes show a distortion in the octahedral geometry.

The fifth chapter describes the synthesis of 16-membered tetraazamacrocyclic complexes of the type, $[MLX_2]$, [M = Co(II), Ni(II), Cu(II) and Zn(II); L = 3,4;7,8;11,12;15,16-tetrabenzo-2,5,10,13-tetraazacyclohexadecane-1,5,9,13-tetraene and X = Cl or NO_3]. The complexes were synthesized from Dichloro/nitrato bis(*o*-phenylenediamine) metal(II) (A) obtained from *o*-phenylenediamine and $MX_2{\cdot}nH_2O$ by reacting with o-phthalaldehyde (1:2 molar ratio) in MeOH solution. However, the ligand [L] has been synthesized by demetallation procedure. The preliminary information regarding the formation of ligand and their complexes has been obtained by the absence of bands around ~3400 cm^{-1} and 1650 cm^{-1} corresponding to νNH_2 and δNH_2 for free primary diamine and the absence of band ca ~1700 cm^{-1} characteristic of ν(C=O) of aldehydic moiety and appearance of a strong intensity band at 1620 cm^{-1} attributable to ν(C=N) in their IR

spectra suggesting the condensation of amino group by aldehydic group. A negative shift of about 20-30 cm^{-1} indicates the involvement of imine nitrogen in coordination to metal ions. The thermogravimetric analysis results account for the relative stabilities of Ni(II) and Cu(II) complexes and the presence of coordinated chloride and nitrate ions. Analytical data correspond to stoichiometry as $[M(C_{28}H_{20}N_4)X_2]$ for the complexes. The electrical conductance of soluble complexes measured in DMSO show their non-electrolytic nature. The Job's method of continuous variation has been used to determine metal to ligand ratio for copper and cobalt complexes which appear at λ= 600 and 500 nm respectively. The same profile was observed when the diagram was constructed at different wavelengths. The bands observed in the electronic spectra of Co(II), Ni(II) and Cu(II) complexes indicate the octahedral geometry around the metal ions. The observed magnetic moments for Co(II), Ni(II) and Cu(II) complexes fall in agreement with their electronic spectral data. A singlet at δ8.05 ppm in the ^1H NMR spectrum of $[ZnLCl_2]$ complex further corroborates the IR spectral findings conforming that the condensation between primary amine and a carbonyl group has occurred leading to the formation of a macrocyclic framework. The spectrum further shows four multiplets at δ6.89, δ7.20, δ7.31 and δ7.50 ppm assignable to the protons of the benzenoid rings.

However, a slight upfield shift has been noticed in free macrocyclic ligand in ^{1}H resonances. The antibacterial activity performed on complexes of Co(II), Ni(II), Cu(II) and Zn(II) against *Escherchia coli, Staphylococcus aureus and Cornybacterium diptheriae* was studied. DMSO was used as a negative control and Streptomycin as a standard drug. The results of this study reveal that all the complexes are active against these microorganisms.

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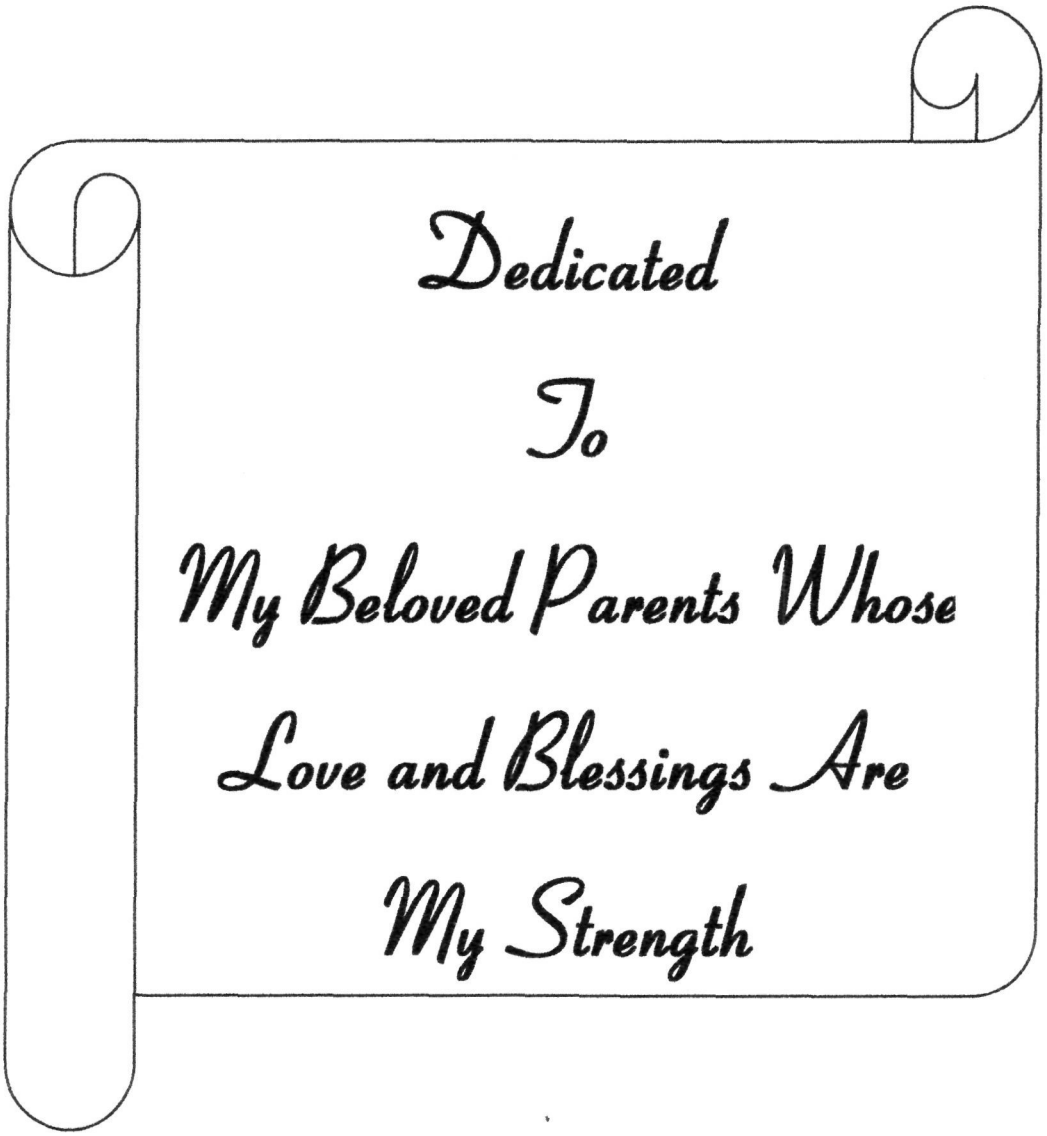
Certificate

Certified that the work embodied in this thesis entitled **"Synthesis and characterization of novel macrocyclic ligands containing N, O or S donor atoms and their complexes"** is the result of original researches carried out by **Ms. Hamida-Tun-Nisa Chisti** under my supervision and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University, Aligarh, India.

01.04.2006

(Prof. Mohammad Shakir)


Dedicated
To
My Beloved Parents Whose
Love and Blessings Are
My Strength

Acknowledgements

First and foremost I would like to bow down my head in front of ***ALMIGHTY*** *the most beneficent, the merciful for making this task reach its completion.*

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My present status in life, this PhD included, is the result of extraordinary will, efforts and sacrifice of my parents. I am unable to find words to express my gratitude and indebtness to them, for their keen interest in my academic persuits, for their faith and their unabounded love. The blessings of my parents have always maintained my enthusiasm throughout my work. I wish them all happiness. It is indeed a privilege to put on my record, the constant encouragement, inspiration and support I received from my sister Dr. Zahida and my brother-in-law Dr. Asif. They have inspired me to always reach for higher horizons. Many thanks to Ms. Nahida who has buffered my ups and downs with unquestioning support. My youngest sister Ms. Shayista is thanked for her continuous love and emotional support. I thank GOD for blessing me with such an understanding and supportive family.

Years spent in Aligarh Muslim University will be cherished. Thankyou Aligarh for showing me the way and lighting the lamp of knowledge in my path.

Thanks to all of you, and with my open heart I pray ***GOD BLESS YOU ALL.***

Hchisht

Hamida-Tun-Nisa Chisti

LIST OF PUBLICATIONS

- Synthesis and physico-chemical studies on 14- and 16- membered octaazamacrocyclic complexes derived from hydrazine with Co (II), Ni (II), Cu (II) and Zn (II).
  Synth. React. Inorg. Met.-Org. Chem., 2003, **33(9)**, 1569-1583.

- Synthesis and characterization of hexaazamacrocyclic complexes with Co(II), Ni(II), Cu(II) and Zn(II) derived from phthalaldehyde and 2,6-Diaminopyridine.
  Synth. React. Inorg. Met.-Org. Chem., 2004, **34(4)**, 809-818.

- Metal ion-directed Synthesis of 16-membered tetraazamacrocyclic complexes and their Physico-chemical studies.
  Spectrochimica Acta Part A, 2005, **64**, 512-517.

CONTENTS

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CHAPTER-I

REVIEW OF LITERATURE

The long awaited renaissance in inorganic chemistry finally arrived during the 1940s and since that time there has been great activity in all branches of the science, particularly in the chemistry of coordination compounds. Historically the concept of coordination chemistry was associated with complexation of a metal cation (Lewis acid) by a ligand (Lewis base). Such was traditionally the case for macrocyclic molecules as ligands. In the early 1970s, however, the concept of coordination chemistry was extended in the area of macrocyclic chemistry. The study of macrocyclic chemistry represents a major area of activity, which impinges on a range of other areas in both chemistry and biochemistry. The field has characteristically yielded many interesting and unusual compounds. The synthesis of macrocycles is an art in itself. A macrocycle is defined as a cyclic molecule with three or more potential donor atoms in a heteroatom ring of atleast nine atoms[1]. Charles J. Pedersen's publication[2] in 1967, "synthesis and characterization of over 30 new cyclic polyether macrocycles" initiated tremendous and continuing interest in the scientific community. This interest was stimulated by the possibilities macrocycles offered to the creative chemist to investigate molecular recognition in new ways. The interest in design of novel macrocyclic ligands stems out mainly in view of their use as models to study magnetic exchange phenomena[3], as sensitizer for

photodynamic therapy[4,5] (PDT) in cancers, as therapeutic reagents[6] in chelate therapy for the treatment of metal intoxication, as synthetic ionophores[7,8], as novel antibiotics[9,10] that owe their antibiotic actions to specific metal complexation, as efficient contrast agents[11,12] for magnetic resonance imaging (MRI). The macrocycles have also been used for the treatment of AIDS, stem cell mobilization[13], to study the host-guest interactions and in catalysis[8,14,15]. Macrocyclic molecules display unique and exciting chemistries in that they can function as receptors for substrates of widely differing physical and chemical properties which can be drastically altered upon complexation. Receptor capabilities are inescapably correlated with the design of a given ligand. Several classes of macrocyclic ligands have been synthesized with varying combinations of aza (N), oxa (O), sulfa (S), and phospha (P) ligating atoms which can be tailored to accommodate specific metal ions by the fine-tuning of the ligand design features, such as the macrocyclic hole size, nature of the ligand donors, donor set, donor array, ligand conjugation, ligand substitution, number and sizes of the chelate rings, ligand flexibility and nature of the ligand backbone. An extensive series of macrocyclic ligands have been synthesized and studied during the last 2-3 decades which are classified into various subdivisions[16] [Figure 1.1 (I-XVIII)]:

i. Coronands[17,18] (I) and (II) are macrocyclic species which contain various heteroatoms as binding sites. The complexes of these ligands are referred to as coronates.

ii. Crown ethers[19] (III) and (IV) are macrocyclic polyethers.

iii. Podandocoronands[20] (V) are macrocyclic ligands with pendant podand chains laterally attached.

iv. Macrocyclic polycarbonyls are cyclic ligands containing carbonyl functionalities- the macrocyclic oligoketones[21] (VI), the polyactones[22] (VII) and the polyactams[23] (VIII).

v. Spherands[24] (IX) and hemispherands[25] (X) are macrocyclic ligands which consist of arrangements of phenyl groups.

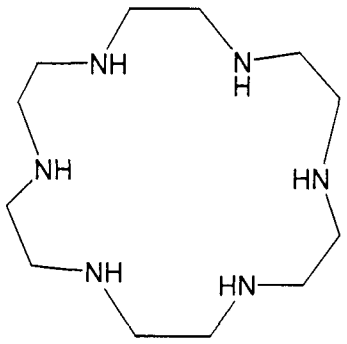
vi. Calixarenes[26] (XI) are macrocyclic phenol-formaldehyde condensation products.

vii. Catapinands[27] (XII) are diazabicycloalkanes.

viii. Catenands[28] (XIII) are two separate, but interlocked macrocyclic ligands.

ix. Cryptands[29-31] (XIV) and (XV) are macropolycyclic receptor molecules which provide a cavity for inclusion of a variety of

substrates. The thermodynamic stabilities of the cryptate complexes strongly depend on the match of the cation size and cryptand cavity diameters[32-35].



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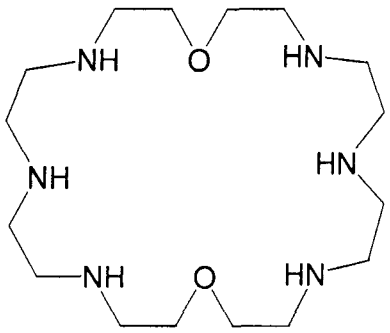

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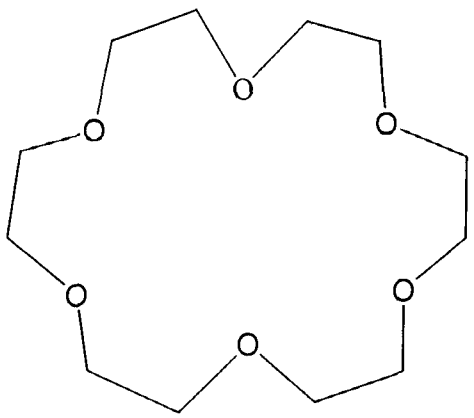

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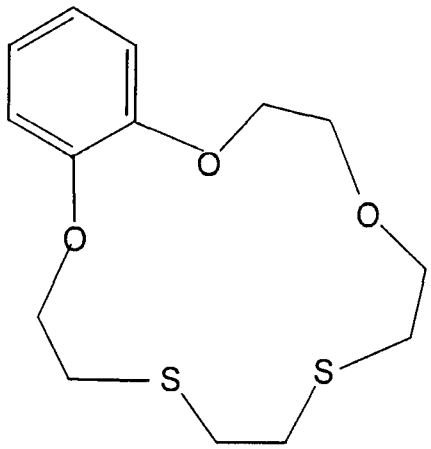

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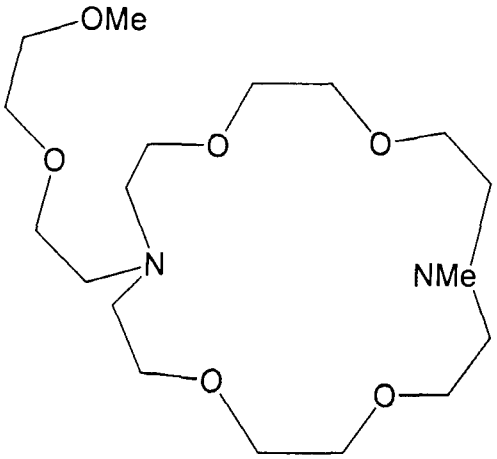
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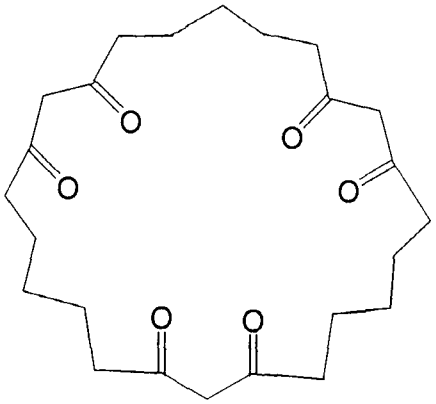
V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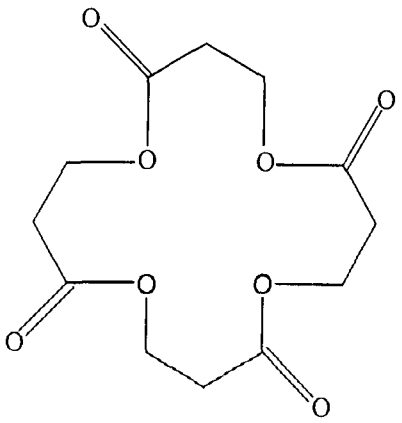
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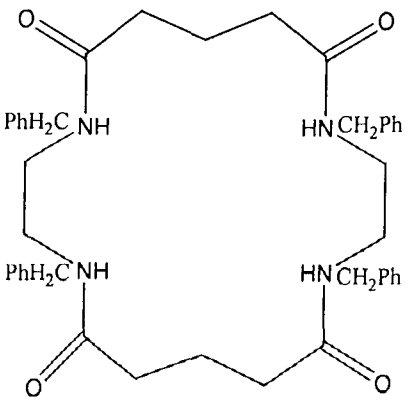
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PhH2C NH
HN CH2Ph
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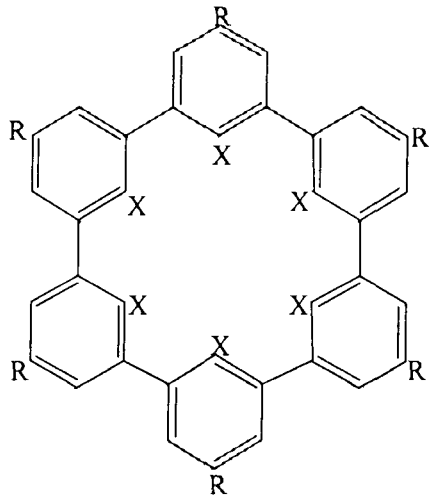
VIII



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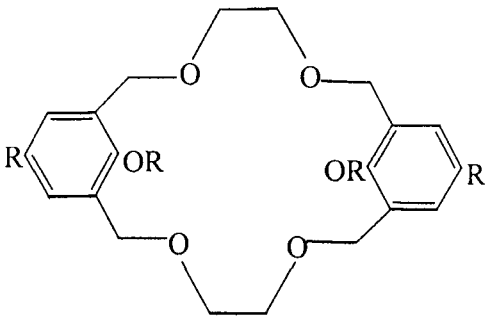
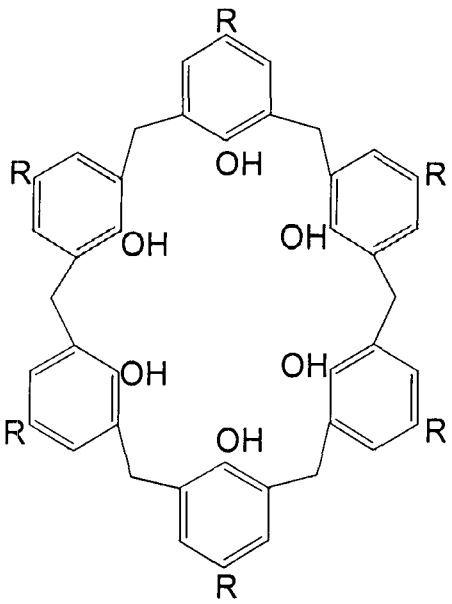
R = Me

IX



R = Me

X



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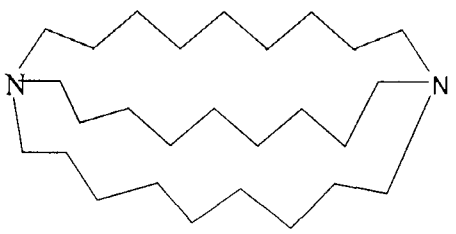
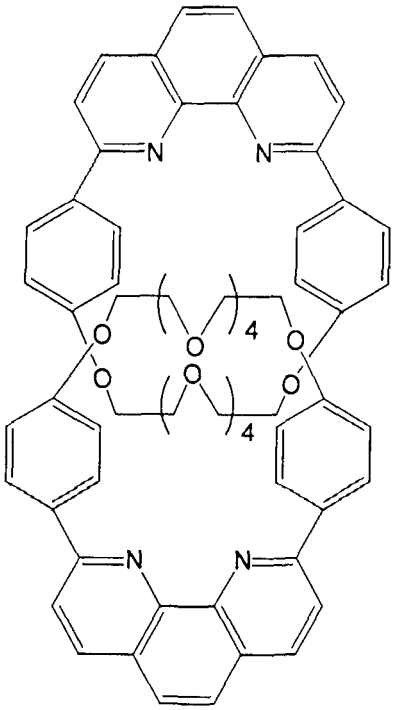
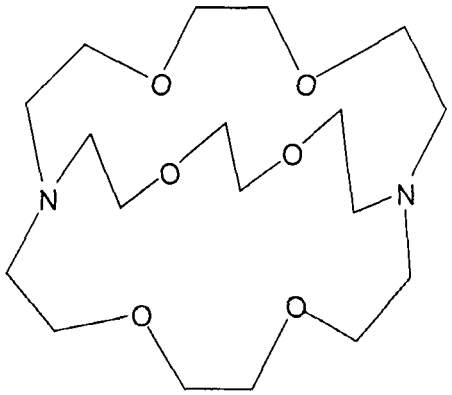


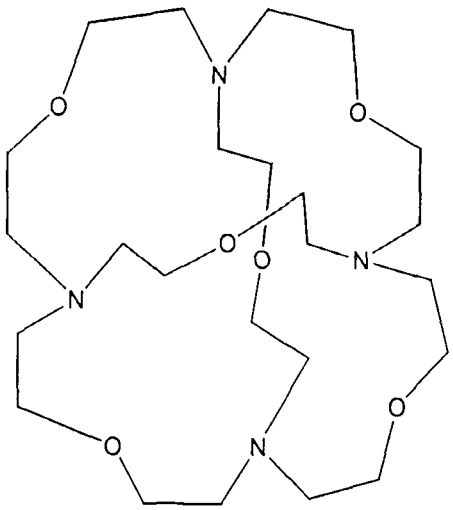
XII



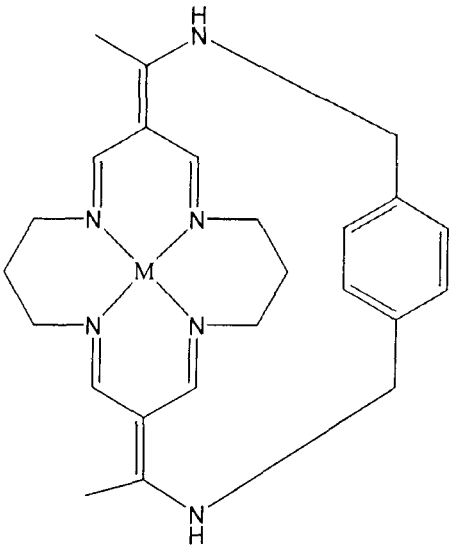
XIII



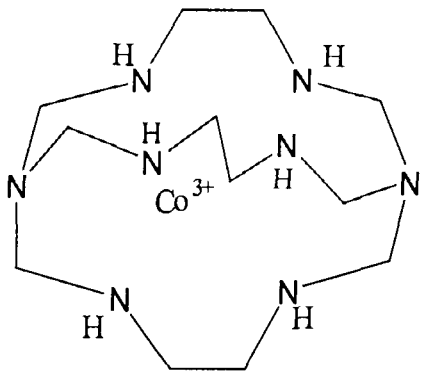
XIV



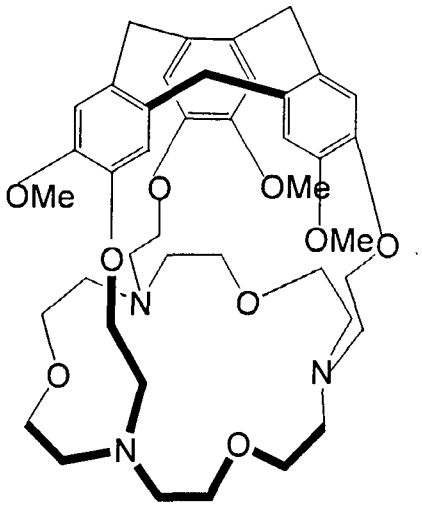
XV



XVI



XVII



XVIII

Figure 1.1 (I - XVIII)

x. Cyclidenes[36] (XVI) are bicyclic macrocycles which coordinate one metal ion and contain a protected "void" about the axial site of the metal ion.

xi. Sepulchrates[37] (XVII) are polyaza macrobicycles analogous to the cryptands.

xii. Speleands[38] (XVIII) are hollow, macropolycyclic molecules formed by the combination of polar binding units with rigid shaping groups.

The compounds shown in Figure 1.1 differ in type and number of ion binding sites and thus generally exhibit quite different affinities for

a given metal ion. For example, certain cyclic polyethers not only strongly bind particular alkali and alkaline earth metals but selectively bind one or more of these ions in preference to the others in each series.

There are four main approaches to prepare such macrocyclic ligand systems:

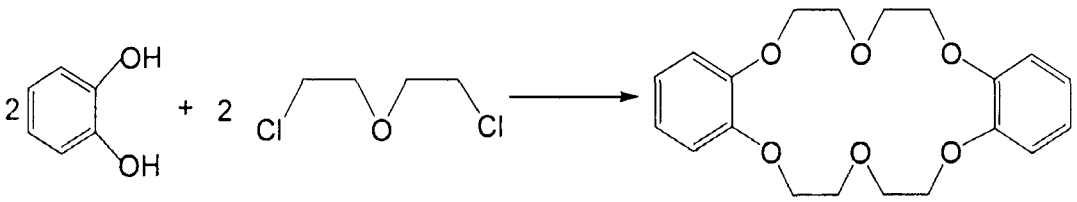
a) Conventional organic synthesis.

b) Metal ion promoted reaction-involving condensation of noncyclic components in the presence of suitable metal ion (in short termed as metal template procedure).

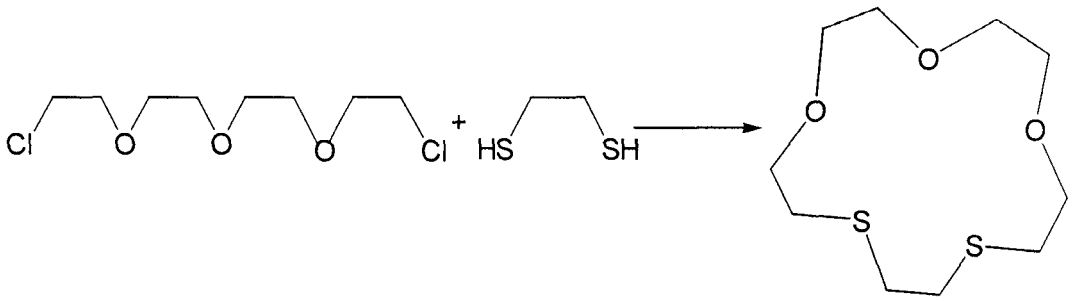
c) Modification of a compound prepared by methods a and b.

d) High dilution technique.

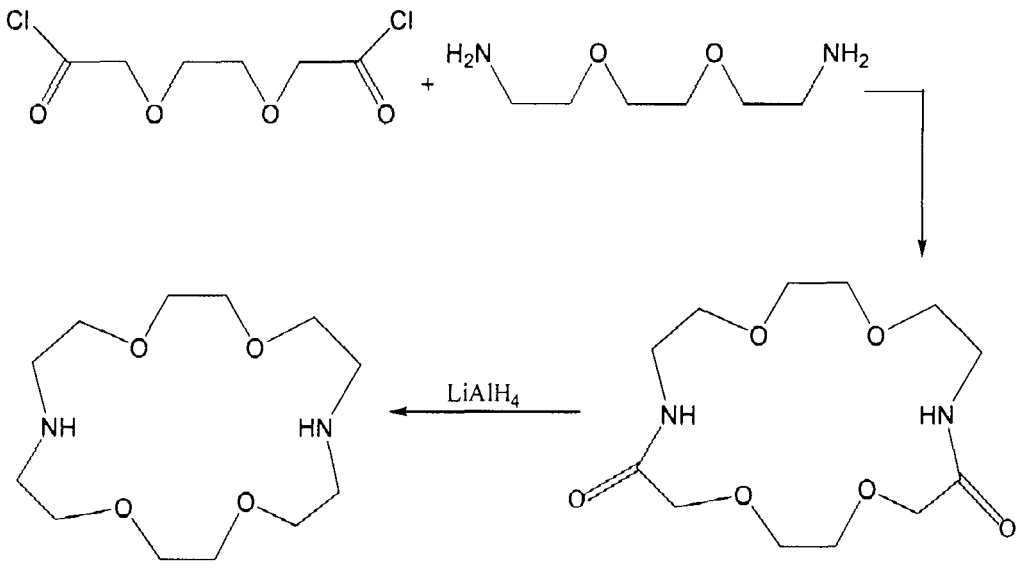
A variety of crown poly-ethers, mixed oxa-thia crowns and oxa-aza crowns have been prepared mainly by the direct synthesis[39-43] (Scheme 1-3).



Scheme 1

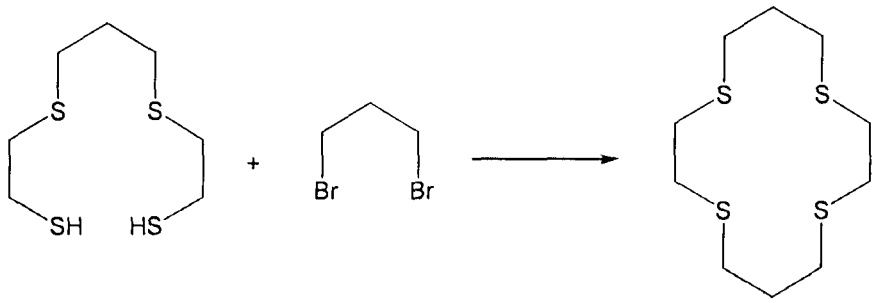


Scheme 2

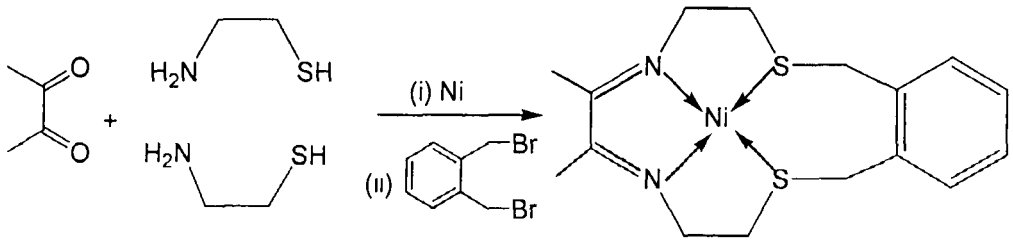


Scheme 3

Polythia macrocycles, have been synthesized by reacting an appropriate polythiane with a dibromoalkane (Scheme 4 and 5). The reactions may sometimes be aided by metal template[44,45].

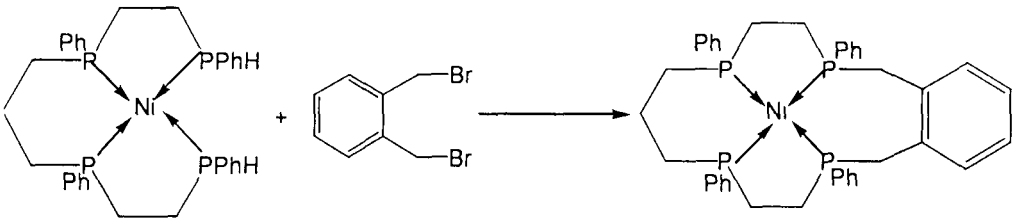


Scheme 4



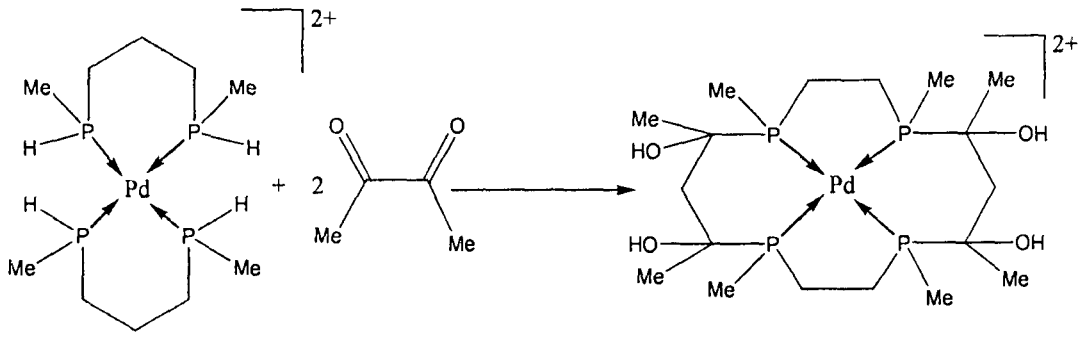
Scheme 5

The phosphorous macrocycles[46] have been made via template condensation of coordinated polyphosphine ligands and a dibromoalkane (Scheme 6).



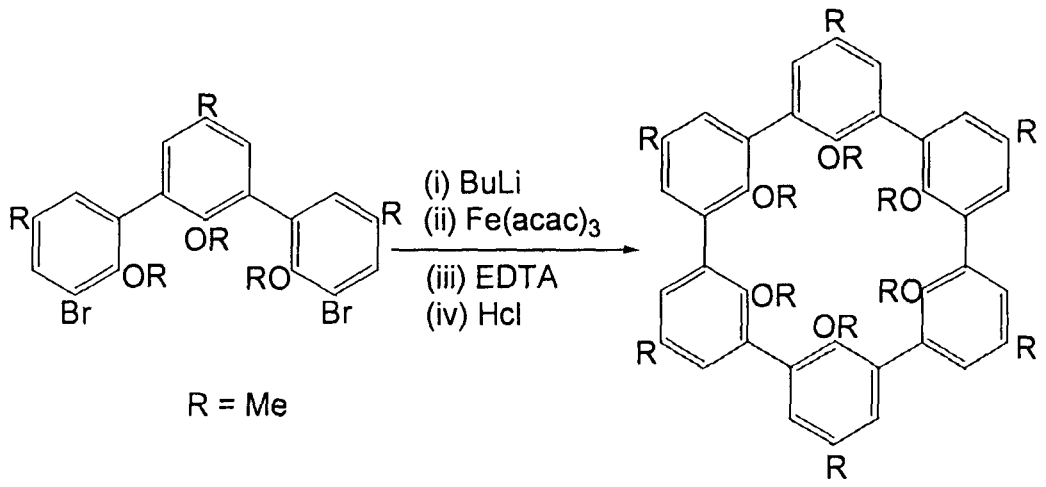
Scheme 6

Template assisted single-stage ring closure methods have also been reported[47] (Scheme 7).



Scheme 7

The synthesis of spherands involves ring closures using aryllithium with $Fe(acac)_3$. However, the yields increases by adopting high dilution techniques[24,48] (Scheme 8).



Scheme 8

A great variety of azamacrocyclic complexes have been formed by condensation reactions in the presence of metal ions (template effect). The majority of such reactions have imine formation as ring closing step. Tetraazamacrocycles with 14- and to a lesser extent, 16-membered predominates and Ni(II) and Cu(II) are the most widely active metal ions used in template procedure[49]. The design and synthesis of organic substrates that preferentially interact with particular metal ion is of fundamental importance to many areas of chemistry. Metal complex stability will be influenced by a range of factors, including:

1. The number and nature of the donor atoms and their spatial arrangements.

2. The backbone structure of the ligand and its ability to accommodate the preferred coordination geometries of the respective metal ions[50] (including the degree of 'preorganisation' present in the system).

3. The number and size of the chelate rings formed on complexation.

4. Crystal field effects of the type underlying the Irving-Williams Stability order[51] for transition metal ions.

The enhanced stability of metal complexes of macrocyclic ligands over other linear polydentate ligands is attributed to various structural effects namely, macrocyclic effect, chelate effect, cryptate effect. These effects which have been found to give stable complexes arise from the structural factors, viz., size, shape or geometry, connectedness or topology and rigidity of the macrocycle. Figure 1.2 displays the general observation that the affinity between the ligands of a particular kind, e.g., amines for a given metal increases with the increasing topological constraint[52] of the ligand system.

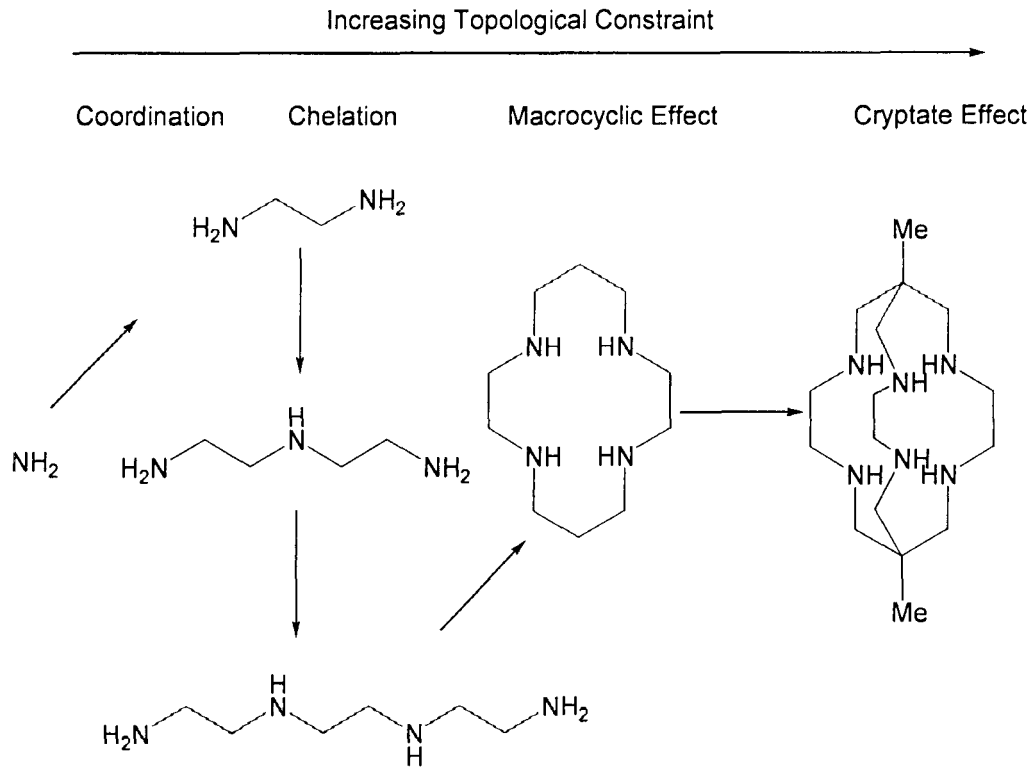
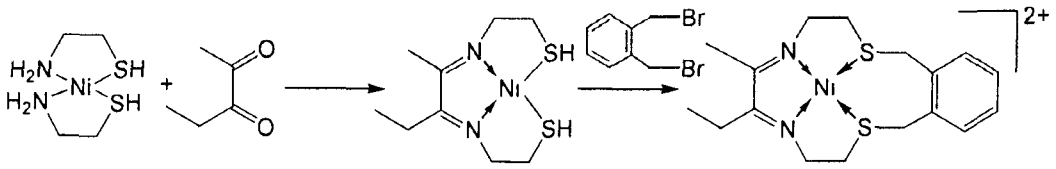


Figure 1.2 Topology and the Chelate, Macrocycle and Cryptate Effect

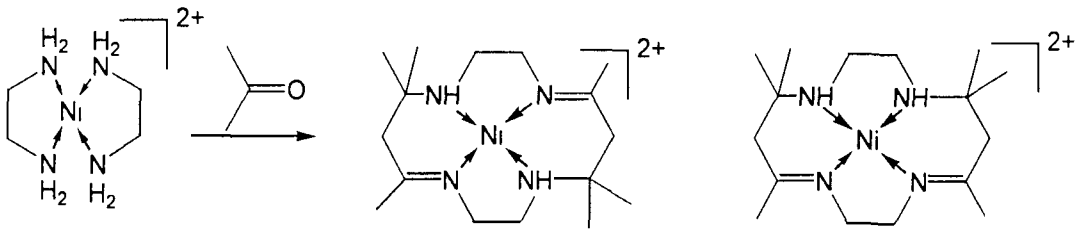
Relative to the open-chain analogues, macrocyclic ligands have further stereochemical constraints associated with their cyclic nature which may influence their potential for metal-ion recognition[53]. The several ligands coordinated to a metal ion are held in specific geometric orientations, and recognition of this fact led to the "coordination template hypothesis"[54,55]. Macrocyclic ligands capable of complexing a variety of metal ions are of considerable interest because of their exceptional inertness to kinetic substitution, thermodynamic stability and electron transfer properties of their complexes[56,57]. Macrocyclic ligands allow selective complexation and extraction of metallic cations and anions of environmental importance[58-61]. The accidental liberation of mercury in the environment posing dreadful toxicity problems, may be solved by the use of macroligands[62-65] containing sulfur which entraps this metal particularly. The macrocyclic effect results in strongly variable thermodynamic and kinetic stability, offering a further opportunity for tuning properties crucial for biological applications such as paramagnetic contrast agents in magnetic resonance imaging particularly lanthanide complexes[66,67], therapeutic radiolabelled conjugates of tumor-localizing molecules specially with trivalent radionuclides[68,69] and sequestering agents for toxic heavy metals such as lead, cadmium and mercury[70]. Macrocyclic complexes of lanthanides have many medicinal applications

such as radioimmunoscintigraphy[71,72] (γ-scintigraphy), as contrast enhancing agents in magnetic resonance imaging[73-77], as NMR shift reagents[78-81] and other clinical applications.

Synthesis of multidentate macrocyclic ligands by the metal template method has been recognized as offering high-yielding and selective routes to new ligands and their complexes[82-86]. The first example of deliberate synthesis of a macrocycle using this procedure was described[87] by Thompson and Busch (Scheme 9) although Curtis had previously demonstrated the potential of template assembly by the reaction of $[Ni(en)_3]$ $(ClO_4)_2$ (en = 1,2-diaminoethane) and acetone yielding isomeric tetraazamacrocyclic complexes[88] of Ni(II) (Scheme 10).

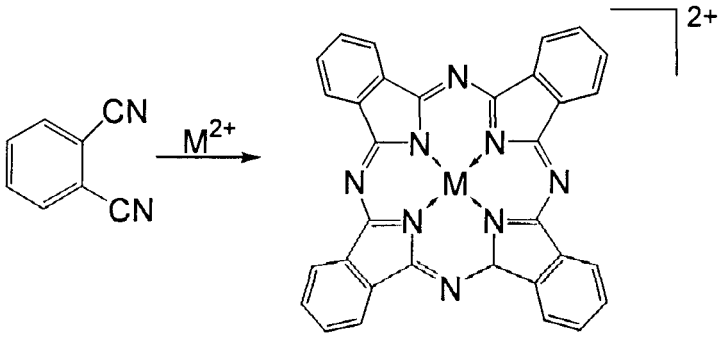


Scheme 9



Scheme 10

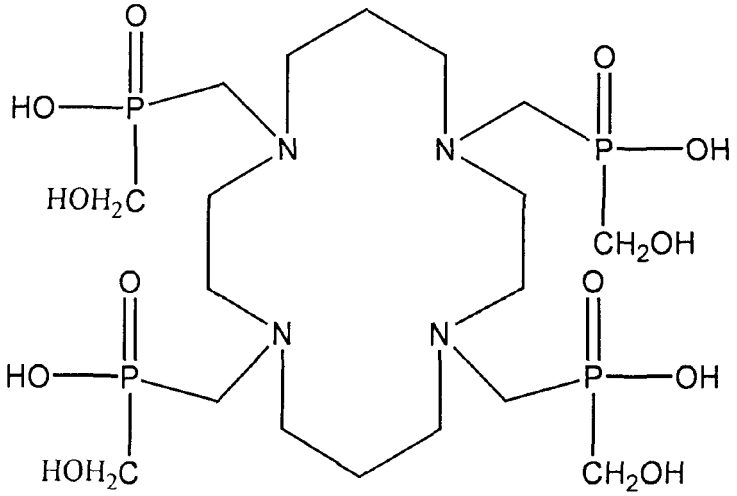
Metal ions also facilitate the self-condensation of o-phthalonitrile to give metal-phthalocyanin complexes[89] (Scheme 11). Shakir and co-workers have reported[90] the self- condensation reaction of o-aminobenzoic acid in the presence of transition metal ions as templates.



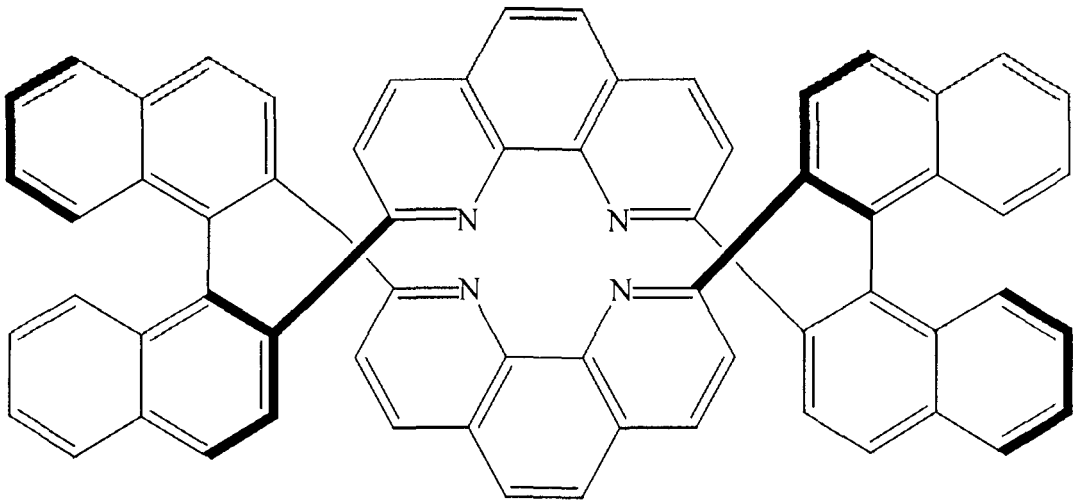
Scheme 11

Polyazamacrocyclic ligands are found to be very versatile ligands due to their capability of forming stable metal complexes[91,92]. Metal coordination by polyazamacrocycles has been widely investigated in the design of selective complexing agents, ionophores and catalysts[93,94]. These compounds have also been used to mimic the active center of important metal containing enzymes[95,96]. Moreover, polyamine macrocycles constitute an excellent basis for the study of molecular recognition of different kinds of substrates, such as inorganic or organic cations[97-100], anions[101-104], and neutral molecules[105]. Among the polyazamacrocycles, tetraazamacrocycles are extensively studied

(Figure 1.3 a and b). To fully encircle a first row transition metal ion a macrocycle-ring size of between 13- and 16 members is required provided that the nitrogen donors are spaced such that five-, six-, or seven-membered chelate rings are produced on coordination[106,107]. Bosnich and co-workers reported[108,109] studies on complexes of tetraazamacrocyclic ligands (Figure 1.4) exhibiting exceptional properties due to the cyclic nature of these ligands which are the cyclic counterpart to alkyl amines. The saturated nitrogens are relatively hard and interact with metal ion through σ bonds. The structural studies are related in terms of various effects such as chelate ring size, degree of unsaturation, and the charge on the coordination number, spin state, redox behaviour and other properties specially of iron derivatives of these macrocyclic ligands. Shakir and co-workers have reported[110-114] the synthesis and characterization of a large number of tetraazamacrocyclic complexes formed by the template condensation.

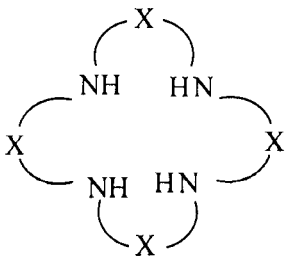


a



b

Figure 1.3



$X = (CH_2)_n$, (n = 2 and 3)

Figure 1.4

Ligands incorporating sulfur donors, form complexes with metals of larger ionic radii, provided that ring sizes should be greater than 13 members inorder to surround the metal ion[115]. A number of larger ring macrocycles containing more than four donor atoms have also been prepared[116-118] (Figure 1.5 and Figure 1.6).

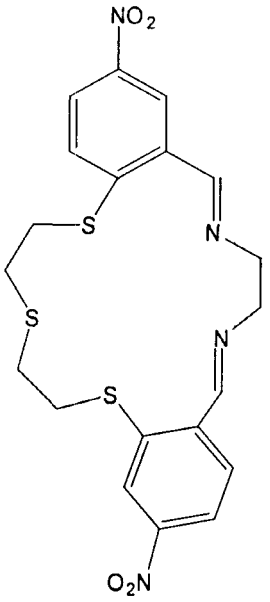


Figure 1.5

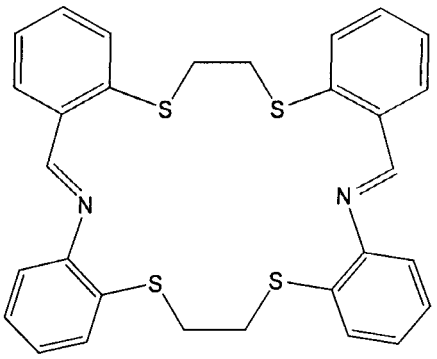
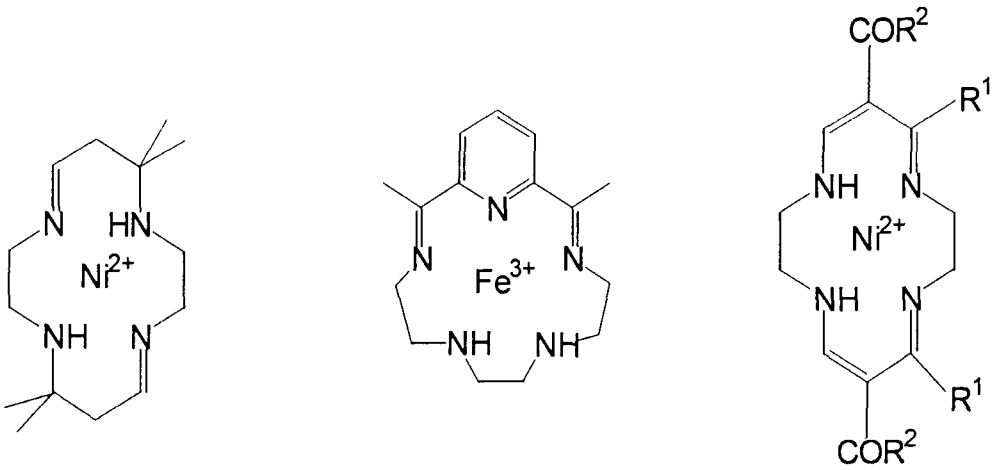


Figure 1.6

Macrocycles containing Schiff base linkages have provided a variety of polydentate macrocycles. The earliest example of a synthetic macrocyclic ligand containing an imine linkage stems from the work of Curtis and was derived from the mixed-aldol condensation of acetone with nickel(II)ethylenediamine complexes[88]. Curry and Busch reported[119] the iron(II) templated condensation of 2,6-diacetylpyridine with triethylenetetramine to give iron(III) complexes of a pentaazadiaminomacrocycle, and Jager showed[120] that the reaction of β-ketoiminato complexes with 1,2-diaminoethane resulting metal complexes of a tetraazadiimino macrocycle [Figure1.7 (a-c)].

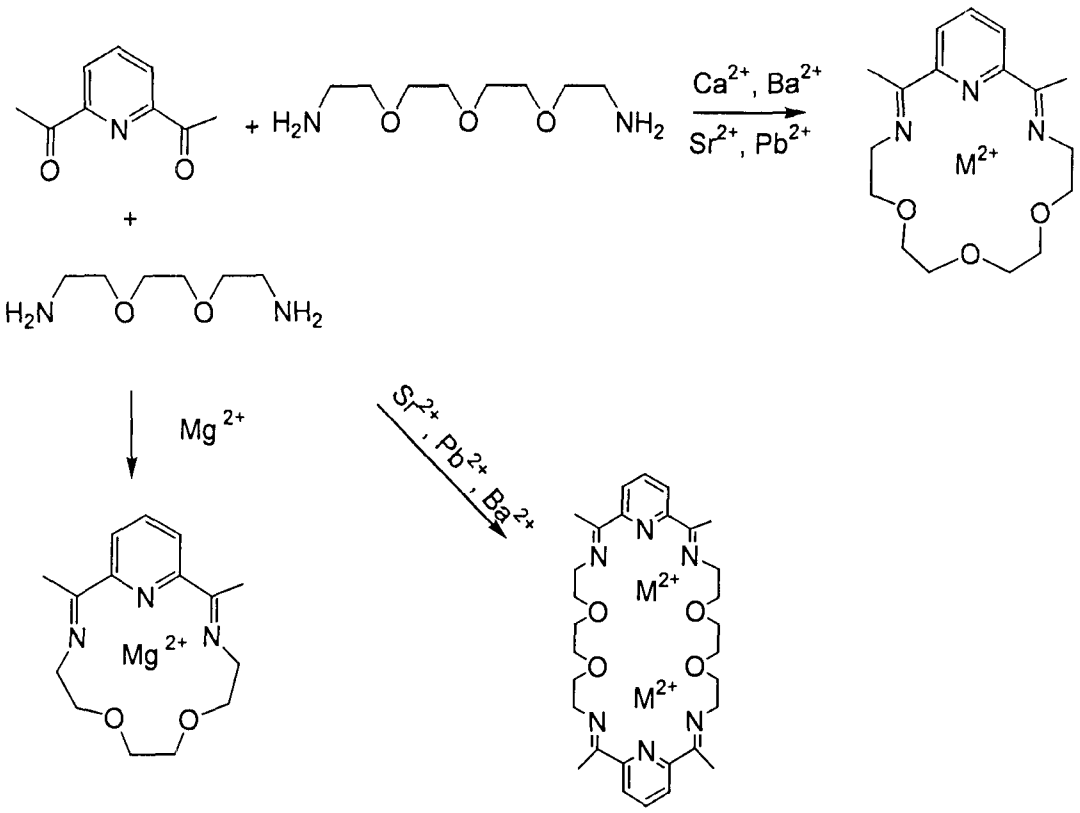


a. Curtis b. Busch c. Jager

Figure 1.7 The Cornerstone Macrocycles

The synthesis of schiff base macrocycles by the template method whether the reaction proceeds by an intramolecular mechanism to give

the "1+1" macrocycle or via the bimolecular mechanism leading to the formation of the "2+2" macrocycle (Scheme 12) depends on one or more of the following factors:



Scheme 12

1. If the diamine has insufficient chain length to span the two carbonyl groups then "1+1" macrocycle cannot be formed[121].

2. If the template ion is large with respect to the cavity size of the "1+1" ring, a "2+2" condensation may occur[122,123].

3. The electronic nature of the metal ion and the requirement of a preferred geometry of the complex.

4. The conformation of the "1+1" acyclic chelate.

5. The smaller metal ion favours the formation of "1+1" while the larger metal ion favours the formation of "2+2" macrocycle.

6. The template potential of a metal ion in the formation of a macrocycle depends on the preference of the cations for stereochemistries i.e, octahedral, tetragonal, square planar or square pyramidal in which the bonding d-orbitals are in orthogonal arrangements. This has been observed when neither copper(II) nor nickel(II) acts as template[124] for the pentadentate "1+1" macrocycles derived by the schiff base condensation of 2,6-diacetylpyridine with triethylenetetraamine or N,N'-bis (3-aminopropyl)ethylenediamine, or N,N'-bis(2-aminoethyl)1,3-propanediamine, respectively.

However, Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} serve as effective templates leading to the formation of seven coordinate complexes of macrocycles[52] (Figure 1.8 a and b). It is therefore, apparent that the metal ion is important to the template process because the size of the cation will determine the degree of dissociation of the metal salt in the reaction medium[125].

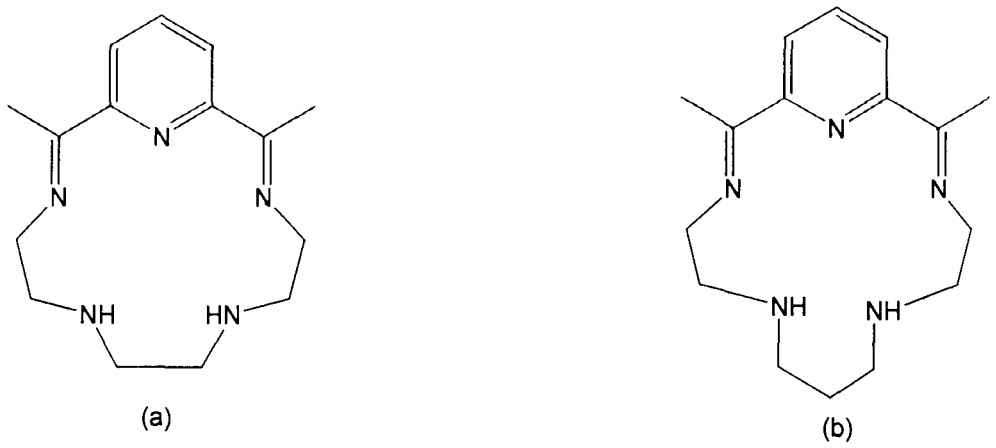
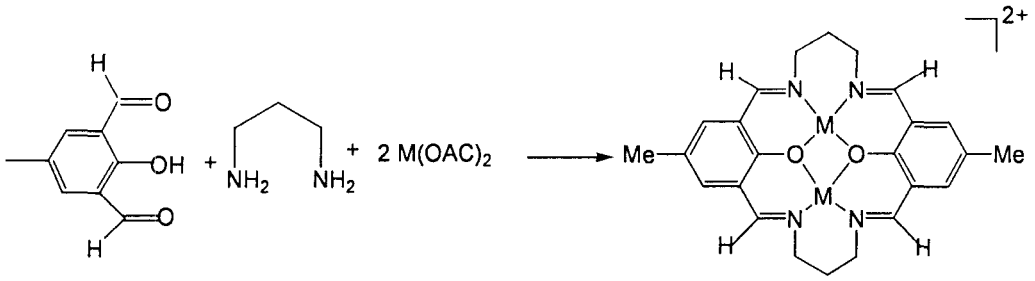


Figure 1.8

The number and relative position of the donor atoms and the cavity size in macrocyclic compounds confer these molecules with special reactivity. From specific dicarbonyl and diamine precursors, the structure of the condensation product can be conditioned by controlling the reaction conditions. Thus, [1+1], [1+2] and [2+2] condensation products, open chain and cyclic structures can be obtained by selecting the appropriate solvent, pH, temperature and the presence of metal ions. Metal salts have been used as templates to yield macrocyclic schiff bases from diamine and dicarbonyl precursors[126,127]. The size of the cation used as the template has proved to be of importance in directing the synthetic pathway for the schiff base systems. The compatibility between the radius of the templating cation and the "hole" of the macrocycle contributes to the effectiveness of the synthetic pathway and to the geometry of the resulting complex[52].

Analogous large-ring ligands have been shown[128-130] to incorporate more than one transition metal ion (Scheme 13).



Scheme 13

The synthesis of the first cryptand (Figure 1.9) in 1968 by Lehn and co-workers[131-133], prompted the synthesis of a large number of macrobicyclic and macropolycyclic compounds and studied their complexation properties.

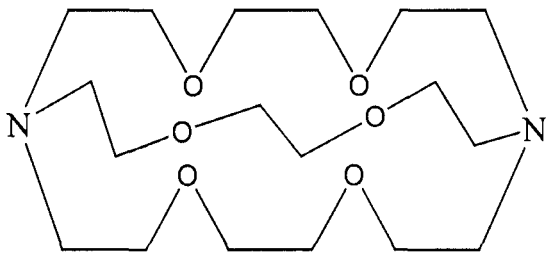
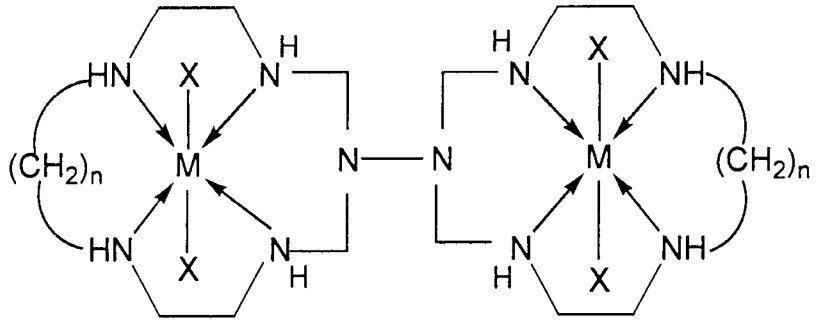


Figure 1.9

A variety of binucleating macrocyclic ligands with similar and dissimilar coordination sites have been reported[134,135] and the later are

of particular interest because such macrocyclic complexes are thermodynamically stabilized and kinetically retarted with regard to metal dissociation and metal substitution relative to metal complexes of acyclic ligand. Shakir and co-workers have reported[136-138] different series of binuclear macrocyclic complexes. Bis(macrocyclic) complexes incorporating two metal ions are of interest because they can act as multi-electron redox agents or catalysts and can be regarded as models for polynuclear metalloenzymes[139]. Furthermore these can exhibit interesting physical properties due to the metal-metal interactions. Shakir and co-workers have recently reported[140] a novel series of pentaazabis(macrocyclic) complexes linked through the N-N bond of hydrazine (Figure 1.10).



(n=2 or 3)

Figure 1.10

The design and synthesis of polyaza macrocycles bearing flexible pendant arms have attracted increasing interest in recent years for the

possible relevance of these compounds as model ligands for metal enzymes and metal proteins as metal ion selective ligands[141,142]. In addition several reports[143-148] have dealt with the synthetic and coordination properties of polyazamacrocycles with pendant N-methylenephosphinic acids. Functionalized macrocycles (Figure 1.11) have been successfully employed in the synthesis of metal chelating agents for medical application owing to the kinetic inertness of the complexes which make them resistant to decomplexation[149,150]. A number of such polydentate ligands have now been reported[151] with a variety of pendant arm macrocycles.

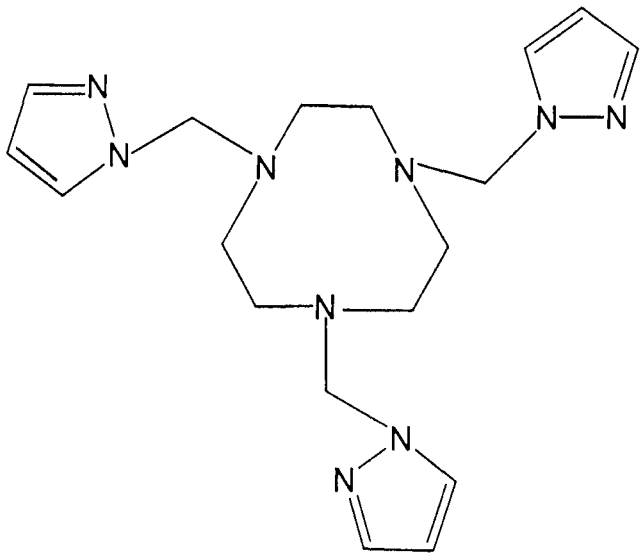
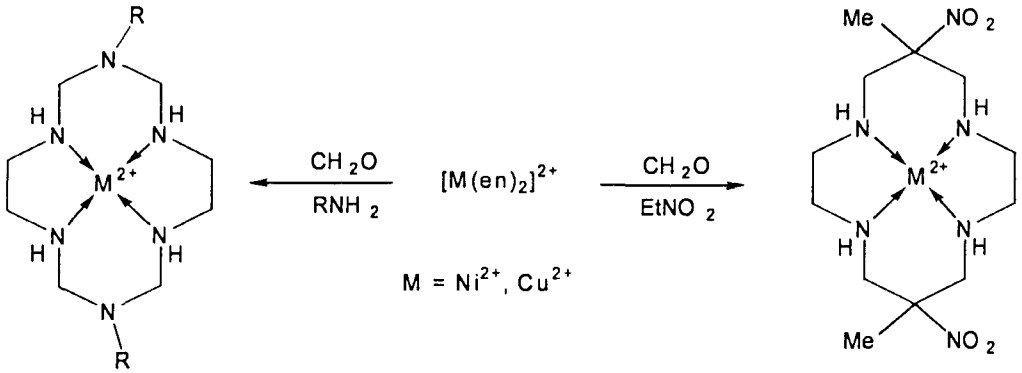


Figure 1.11

Kanda and co-workers discussed the preparation and reaction of a tetradentate schiff base ligand having a pendant thioether function[152].

Busch and co-workers studied[153] a macrocycle with a pendant pyridyl function which is sterically restricted in its binding to the metal centers. Various pendant-armed macrocyclic complexes have also been reported[154-156] by Shakir and co-workers in this laboratory.

It is well established that various macrocyclic complexes have been synthesized by the template condensation of amines with aldehydes in the presence of metal ions, particularly formaldehyde has been utilized for the cyclization to link the amine moieties[157,158]. The reaction of a monocarbonyl compound to yield a macrocyclic product is represented by the condensation of $[Ni(en)_2]^{2+}$ or $[Cu(en)_2]^{2+}$ with formaldehyde in the presence of a suitable nucleophile[159] (Scheme 14).



Scheme 14

This reaction is related to the condensation of $[Co(en)_3]^{3+}$ with formaldehyde in presence of nucleophiles to form clathrochelate compounds and the formation of the Co^{III}[14]ane, $[N_4O_2]$ complex

(Figure 1.12) by reaction of a bis(ethanediamine) cobalt(III) complex with formaldehyde[160].

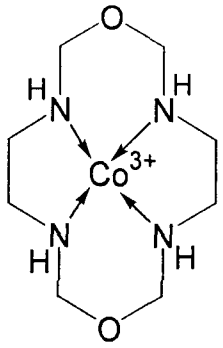


Figure 1.12

A variety of macrocyclic complexes which have adjacent nitrogen atoms (cyclic hydrazines, hydrazone or diazines) are formed by condensation of hydrazine, substituted hydrazines or hydrazones with carbonyl compounds. Tetradentate and pentadentate aza macrocycles are formed[161] by condensation of 2,6-diacetylpyridine with hydrazine (Figure 1.13) or with dihydrazines (Figure 1.14). Shakir and co-workers have reported[162-164] a variety of macrocyclic complexes derived from hydrazine.

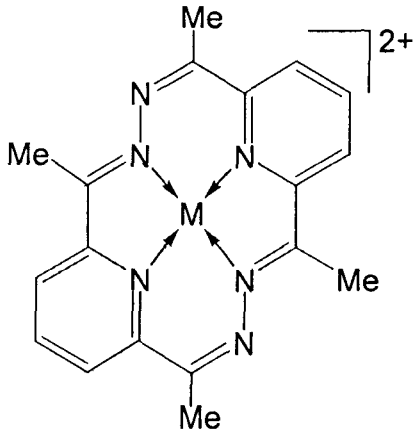


Figure 1.13

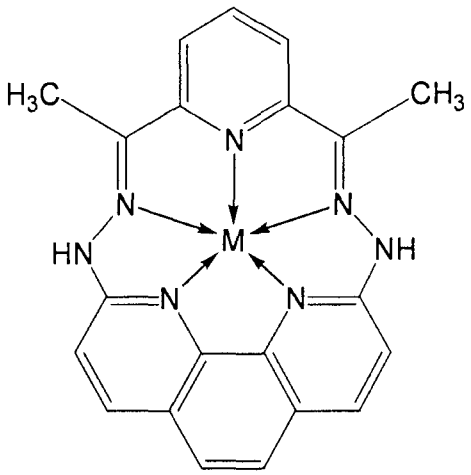


Figure 1.14

Macrocycles especially the ones possessing aromatic moieties are known to form charge transfer complexes with a variety of guests. These macrocycles were used to study complexation of diverse guests to provide new insights into noncovalent binding interactions, chiefly

cation-π interactions[165]. These interactions involve the stabilization of a positive charge by the face of an aromatic ring[166]. The cation-π interactions are important binding forces in biological receptors like acetylcholine. A number of macrocycles have been prepared[167-171] having o-phthaldialdehyde (Figure 1.15), o-phenylenediamine (Figure 1.16) and 2,6-diaminopyridine (Figure 1.17) as structural backbone in the macrocyclic framework.

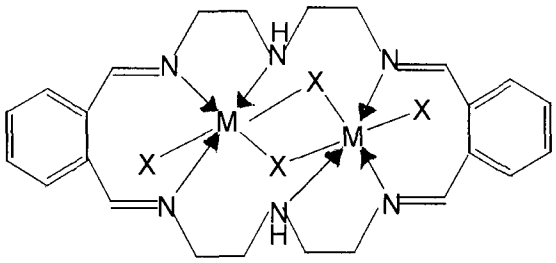


Figure 1.15

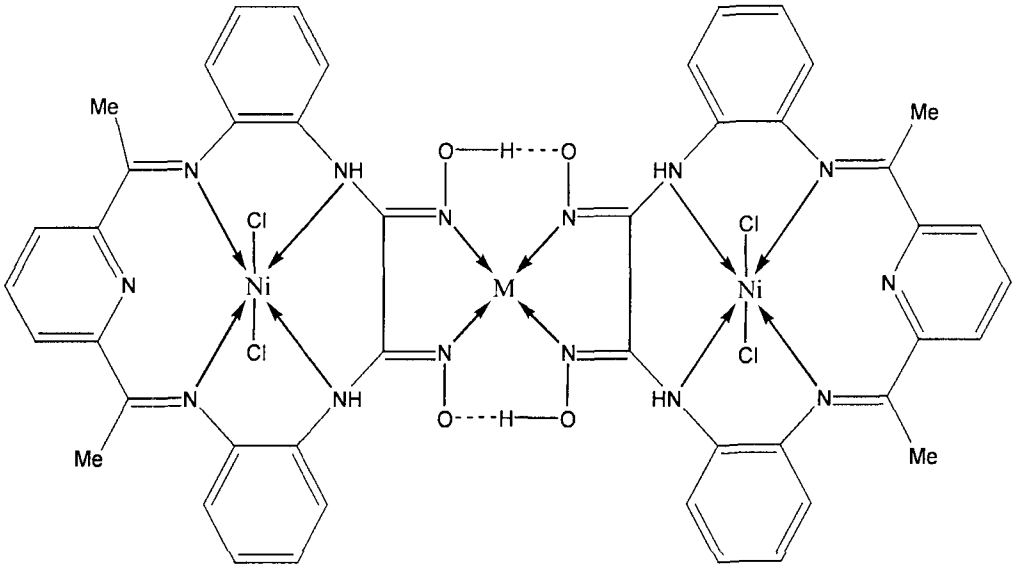


Figure 1.16

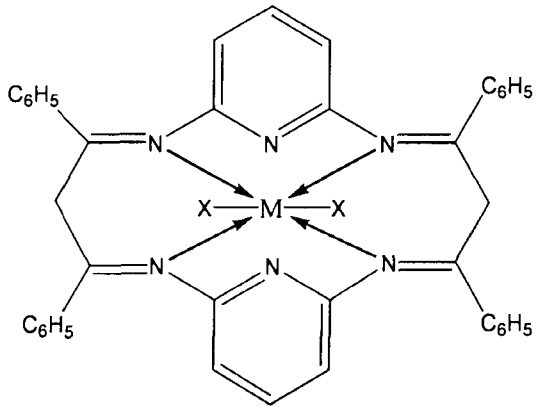


Figure 1.17

In view of the current interest in the field of macrocyclic moieties especially their biological, catalytic and industrial applications it was thought worthwhile to report the design and details of the synthesis and characterization of several novel octaaza, hexaaza and tetraazamacrocyclic complexes encapsulating first row transition metal ions. A few macrocyclic complexes have also been subjected to study their biological application against *E. coli*, *S. aureus* and *C. diptheriae*.

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CHAPTER II

EXPERIMENTAL METHODS

2.1 INSTRUMENTAL METHODS

There are several physico-chemical methods available for the study of coordination and macrocyclic compounds and a brief description of the techniques used in the investigation of the newly synthesized complexes described in the present work are given below:

1- Infrared Spectroscopy

2- Nuclear Magnetic Resonance Spectroscopy

3- Electron Paramagnetic Resonance Spectroscopy

4- Ultraviolet and Visible (Ligand Field) Spectroscopy

5- Magnetic Susceptibility Measurements

6- Molar Conductance Measurements

7- Elemental Analyses

8- Thermogravimetric Analysis

9- Job's method

10- Antimicrobial Activity

2.1.1 *INFRARED SPECTROSCOPY*

When Infrared light is passed through a sample some of the frequencies are absorbed while other frequencies are transmitted through the sample without being absorbed. The plot of the percent absorbance or percent transmittance against frequency, results in an infrared spectrum.

The IR radiation does not have enough energy to induce electronic transitions observed in UV spectroscopy. Absorption of IR radiation is restricted to the compounds with small energy differences in the possible vibrational and rotational states. For a molecule to absorb IR radiation, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a net change in the amplitude of the molecular vibration.

In the absorption of the radiation, only transition for which change in the vibrational energy level is $\Delta V = 1$ can occur, since most of the transition will occur from stable V_o to V_1 the frequency corresponding to its energy is called the fundamental frequency.

The group frequency, which are frequencies of certain groups, are characteristic of the group irrespective of the nature of the molecule in which these groups are attached. The absence of any band in the approximate region indicates the absence of that particular group in the molecule.

The infrared region of the spectrum encompasses radiation with wavenumbers ranging from about 12,800 to 10 cm^{-1} or wavelengths from 0.78 to 1000 μm. In the context of infrared spectroscopy, wavelength is measured in "wavenumbers", which have the units cm^{-1}

Wave number = 1/wavelengh in centimeters

$$\nu = 1/\lambda$$

From the standpoint of both application and instrumentation, the infrared spectrum is conventionally divided into three regions; near-, mid- and far- infrared radiation:

Region	Wavelength range (μm)	Wavenumber range (cm^{-1})
Near	0.78-2.5	12800-4000
Middle	2.5-50	4000-200
Far	50-1000	200-10

Important Group Frequencies in the IR Spectra Pertinent to the Discussion of the Newly Synthesized Compounds.

a) N-H Stretching Frequency

The N-H stretching vibrations occur in the region 3300-3500 cm^{-1} in the dilute solution[1]. The N-H stretching band shifts to lower value in the solid state due to the extensive hydrogen bonding. Primary amines as dilute solutions in non-polar solvents give two absorptions i.e., symmetric stretch and asymmetric stretch mode found near 3400 and

3500 cm^{-1}, respectively. Secondary amines show only a single N-H stretching band in dilute solutions. The intensity and frequency of N-H stretching vibrations of secondary amines are very sensitive to structural changes e.g., it appears as low intensity band in the range 3310-3350 cm^{-1} in aliphatic while as strong intensity band at about 3490 cm^{-1} in heterocyclic secondary amines such as pyrazole and imidazole.

b) C-N Stretching Frequency

The C-N stretching absorption occurs as strong bands in the region 1250-1350 cm^{-1} in all the amines[1,2]. In primary aromatic amines it shows one band in the region 1250-1340 cm^{-1} but in secondary amines two bands have been found in the regions 1280-1350 cm^{-1} and 1230-1280 cm^{-1}.

c) C=N Stretching Frequency

Schiff bases (RCH=NR, imines), oximes, thiazoles, iminocarbonates etc. show the C=N stretching frequency in the 1471-1689 cm^{-1} region[1,2]. Although the intensity of the C=N stretch is variable but it is usually more intense than the C=C stretch.

d) N–N Stretching Frequency

A strong band appearing in the region around 1000 cm^{-1} may reasonably be assigned[3] to ν(N–N) vibrations.

e) Pyridine Ring Vibration

The free pyridine molecule exhibits three important ring vibrations, i.e., 6a and 8a vibrations (in-plane ring deformations) appearing around 601 and 1578 cm^{-1} respectively[4,5] while the 16b vibration (out- of- plane ring deformation) is observed around 403 cm^{-1}. It has been indicated that the positions of the two lower bands and undergo a positive shift upon coordination. The magnitude of the positive shift has been showed to be a function of the stereochemistry and the nature of the metal ions.

f) M-N Stretching Frequency

The M-N stretching frequency is of particular interest since it provides direct information regarding the metal-nitrogen coordinate bond. Different amine complexes exhibited[2] the metal-nitrogen frequencies in the 300-450 cm^{-1} region.

g) M-X Stretching Frequency

Metal-halogen stretching bands appear[2] in the region of 500-750 cm^{-1} for MF, 200-400 cm^{-1} for MCl, 200-300 cm^{-1} for MBr and 100-200 cm^{-1} for MI.

h) M-O Stretching Frequency

Metal-oxygen stretching frequency has been reported to appear in different regions for different metal complexes. The M-O stretching

frequency of nitrato complexes lies in the range 250-350 cm^{-1}. Furthermore unidentate nitrate group display bands around 1430, 1271 and 992 cm^{-1} region assigned[2] to ν(N-O) vibrations.

2.1.2 *NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY*

^{1}H NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is based on the measurement of electromagnetic radiation in the radio-frequency region of roughly 4 to 900 MHz. In contrast to Ultraviolet, Visible, and Infrared absorption, nuclei of atoms rather than outer electrons are involved in the absorption process.

Nuclear magnetic resonance spectroscopy is one of the most powerful tools available to the chemists and biochemists for elucidating the structure of chemical species.

There are two types of NMR spectrometers:

a) Continuous- Wave (CW)

b) Pulsed, or Fourier transform (FT-NMR)

All early studies were carried out with continuous-wave instruments. Fourier transform spectrometers were available commercially around 1970. In both types of instruments, the sample is positioned in a powerful magnetic field that has strength of several teslas. The only nuclei that exhibit the NMR phenomenon are those for

which the spin quantum number I is greater than 0, the spin quantum number I is associated with the mass number and atomic number of the nuclei as follows:

Mass number	Atomic number	Spin quantum number
Odd	odd or even	1/2, 3/2, 5/2, --------
Even	even	0
Even	odd	1,2,3, ---------

The nucleus of ^{1}H, the proton, has I = 1/2, whereas ^{12}C and ^{16}O have I = 0 and are therefore nonmagnetic. Nuclei for which I = 1/2 include ^{1}H, ^{13}C, ^{19}F and ^{31}P, while ^{2}H and ^{14}N have I = 1.

A spinning, charged nucleus creates a magnetic field that is analogous to the field produced when electricity flows through a coil of wire. The resulting magnetic moment μ is oriented along the axis of spin and is proportional to the angular momentum p. Thus,

$$\mu = \gamma p$$

Where, γ is gyromagnetic ratio

Under the influence of an external magnetic field, a magnetic nucleus can take up different orientation with respect to that field, the number of possible orientations is given by (2I+1), so that for nuclei with spin quantum number 1/2, (^{1}H, ^{13}C, ^{19}F, etc.) only two orientations are allowed.

If a proton is precessing in the aligned orientation, it can absorb energy and pass into the opposed orientation, subsequently it can lose this extra energy and relax back into the aligned position. If the precessed nuclei is irradiated with a beam of radiofrequency energy of the proper frequency, the lower energy nuclei will absorb this energy and move to a higher energy state. If the precessing frequency is same as the frequency of the radiofrequency beam, the nucleus and the radiofrequency beam are said to be in resonance, hence the term Nuclear Magnetic Resonance.

NMR spectra can be recorded by either holding the magnetic field constant and scanning the radiofrequency or by keeping the radiofrequency constant and varying the magnetic field. The higher the operating frequency, the better will be the resolution, and thus easier the interpretation.

2.1.3 *ELECTRON SPIN RESONANCE SPECTROSCOPY*

Electron resonance is a branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by molecules possessing electrons with unpaired spins.

Gorter demonstrated[6,7] that a paramagnetic salt when placed in a high frequency alternating magnetic field absorbs energy, which is

influenced by the application of a static magnetic field either parallel or perpendicular to the alternating magnetic field.

For an electron of spin = 1/2, the spin angular momentum quantum number can have values of $m_s = \pm 1/2$, which in the absence of a magnetic field leads to doubly degenerate spin energy state. When a magnetic field is applied, this degeneracy is resolved. The low energy state has the spin magnetic moment aligned with the field and corresponds to the quantum number, $m_s = -1/2$. While the higher energy state, $m_s = +1/2$, has its moment opposed to the field. The energy difference between two spin energy states is predominately due to the interaction of unpaired electrons in the sample with an external magnetic field. This effect is called the Zeeman effect.

A transition between the two different electron spin energy states occurs upon absorption of a quantum of radiation in the radio frequency or microwave region. The energy, E, of the transition is given by:

$$E = h\nu = g\beta H_o$$

Where h is Planck's constant, v the frequency of radiation, β the Bohr magneton, H_o the field strength and g the spectroscopic splitting factor.

The quantity g is not constant but a tensor quantity. For a free electron g has the value of 2.0023. In many free radicals, the g value of the odd electron is close to that of a free electron, but in metal ions g values are often greatly different from the free electron value.

In general the magnitude of g depends upon the orientation of the molecule containing the unpaired electron with respect to the magnetic field.

When an electron comes in the vicinity of a nucleus with a spin I, an interaction takes place which causes the absorption signal to be split into 2I+1 components. The cause of this splitting in an isotropic system is the nuclear spin- electron spin coupling arising mainly from the Fermi contact term.

There may be an additional hyperfine structure also due to interaction between magnetic electrons and the surrounding nuclei called superhyperfine structure. The effect was first observed by Owens and Stevens in ammonium hexa chloroiridate[8] and subsequently for a number of transition metal ions in various hosts[9,10].

2.1.4 ULTRA-VIOLET AND VISIBLE (LIGAND FIELD) SPECTROSCOPY

Most of the compounds absorb light somewhere in the spectral region between 200 and 1000 nm. These transitions correspond to the

excitation of electrons of the molecules from ground state to higher electronic states. In a transition metal all the five d-orbitals viz., d_{xy}, d_{yz}, d_{xz}, d_{z^2} and $d_{x^2-y^2}$ are degenerate. However, in coordination compounds due to the presence of ligands this degeneracy is lifted and d-orbitals split into two groups called t_{2g} (d_{xy}, d_{yz} and d_{xz}) and e_g (d_{z^2} and $d_{x^2-y^2}$) in an octahedral complex and t and e in a tetrahedral complex. The set of t_{2g} orbitals goes below and the set of e_g orbitals goes above the original level of the degenerate orbitals in an octahedral complex. In case of the tetrahedral complexes the position of the two sets of the orbitals is reversed, the e going below and t going above the original degenerate level. When a molecule absorbs radiation, its energy equal in magnitude to hv and can be expressed by the relation:

$$E = h\nu$$

$$\text{or } E = hc/\lambda$$

Where h is Planck's constant, v and λ are the frequency and wavelength of the radiation, respectively and c is the velocity of the light.

In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon 'Russell Saunders Scheme' must be introduced. This has the effect of splitting the highly degenerate configurations into groups of levels having lower degeneracies known as 'Term Symbols'.

The orbital angular momentum of electrons in a filled shell vectorically adds up to zero. The total orbital angular momentum of an incomplete d shell electron is observed by adding L value of the individual electrons, which are treated as a vector with a component ml in the direction of the applied field. Thus,

$$L = \Sigma_i \, ml_i = 0, 1, 2, 3, 4, 5, 6$$

$$S, P, D, F, G, H, I$$

The total spin angular momentum $S = \Sigma_i \, s_i$ where s_i is the value of spin angular momentum of the individual electrons. S has a degeneracy τ equal to $2S + 1$, which is also known as 'Spin Multiplicity'. Thus a term is finally denoted as 'τL'. For example, if $S = 1$ and $L = 1$, the term will be ^3P and similarly if $S = 1\frac{1}{2}$, and $L = 3$, the term will be ^4F.

In general the terms arising from a d^n configuration are as follows:

$d^1 d^9$: ^2D

$d^2 d^8$: $^3F, ^3P, ^1G, ^1D, ^1S$

$d^3 d^7$: $^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P$

$d^4 d^6$: $^5D, ^3H, ^3G, ^3F(2), ^3D, ^2P(2), ^1I, ^1G(2), ^1F, ^1D(2), ^1S(2)$

d^5 : $^4S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2), ^2F(2), ^2D(3), ^2P, ^2S.$

Coupling of L and S also occurs, because both L and S if non-zero, generate magnetic fields and thus tend to orient their moments with respect to each other in the direction where their interaction energy is

least. This coupling is known as 'LS coupling' and gives rise to resultant angular momentum denoted by quantum number J which may have quantized positive values from | L + S | up to | L - S | e.g., in the case of ^3P (L = 1, S = 1), ^4F (L = 3, S = 1 ½) possible values of J representing state, arising from term splitting are 2, 1 and 0 and 4 ½, 3 ½, 2 ½, and 1 ½. Each state is specified by J is 2J + 1 fold degenerate. The total number of states obtained from a term is called the multiplet and each value of J associated with a given value of L is called component. Spectral transitions due to spin-orbit coupling in an atom or ion occurs between the components of two different multiplets while LS coupling scheme is used for the elements having atomic number less than 30, in that case spin-orbital interactions are large and electrons repulsion parameters decreases. The spin-angular momentum of an individual electron couples with its orbital momentum to give an individual J for that electron. The individual J's couple to produce a resultant J for the atom. The electronic transitions taking place in an atom or ion are governed by certain 'Selection Rules', which are as follows:

1. Transitions between states of different multiplicity are forbidden.
2. Transitions involving the excitation of more than one electron are forbidden.

3. In a molecule, which has a centre of symmetry, transitions between two gerade or two ungerade states are forbidden.

It is possible to examine the effects of crystal field on a polyelectron configuration. The ligand field splitting due to cubic field can be obtained by considerations of group theory. It has been shown that an S state remains unchanged. P states does not split, and D state splits into two and F state into three and G state into four states as tabulated below: (Applicable for an octahedral 'Oh' as well as tetrahedral 'Td' symmetry).

S ----------A_1

P ----------T_1

D ---------- $E + T_2$

F ---------- $A_2 + T_1 + T_2$

G ---------- $A_2 + E + T_1 + T_2$

Transitions from the ground state to the excited state occur according to the selection rules described earlier. The energy level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse that of the ion in a tetrahedral field. However, due to transfer of charge from ligand to metal or metal to ligand, sometimes bands appear in the ultraviolet region of the spectrum. These spectra are known as 'Charge Transfer Spectra' or

'Redox Spectra'. In metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transition. However, these should be clearly discerned from the ligand bands, which might also occur in the same region.

2.1.5 *MAGNETIC SUSCEPTIBILITY MEASUREMENTS*

The determination of magnetic moments of transition metal complexes has been found to provide ample information in assigning their structure. The main contribution to bulk magnetic properties arises from magnetic moment resulting from the motion of electrons. It is possible to calculate the magnetic moments of known compounds from the measured values of magnetic susceptibility.

There are several kinds of magnetism in substances viz., diamagnetism, paramagnetism and ferromagnetism or antiferromagnetism. Mostly compounds of the transition elements are paramagnetic. Diamagnetism is attributable to the closed shell electrons with an applied magnetic field. In the closed shell the electron spin moment and orbital moment of the individual electrons balance one another so that there is no magnetic moment. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighboring atoms.

If a substance is placed in a magnetic field H, the magnetic induction B with the substance is given by:

$$B = H + 4\pi I$$

Where I is the intensity of magnetization. The ratio B/H is called magnetic permeability of the material and is given by:

$$B/H = I + 4\pi(I/H) = I + 4\pi K$$

Where K is called the magnetic susceptibility per unit volume or volume susceptibility. B/H is the ratio of the density of lines of force within the substance to the density of such lines in the same region in the absence of sample. Thus, the volume susceptibility of a vacuum is by definition zero since in vacuum B/H = 1.

When magnetic susceptibility is considered on the weight basis, the gram susceptibility (χ_g) is used instead of volume susceptibility. The μ_{eff} value can then be calculated from the gram susceptibility multiplied by the molecular weight and corrected for diamagnetic value as:

$$\mu_{eff} = 2 \cdot 84\sqrt{\chi_M^{corr} \cdot T}\ BM$$

Where T is the absolute temperature at which the experiment is performed.

The magnetic properties of any individual atom or ion will result from some combination of these two properties that is the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus. The magnetic moments are

usually expressed in Bohr Magnetons (BM). The magnetic moment of a single electron is given by:

$$\mu_S = g\sqrt{S(S+1)}\,BM$$

Where S is the spin quantum number and g is the gyromagnetic ratio. For Mn^{2+}, Fe^{3+} and other ions whose ground states are S states there is no orbital angular momentum. In general however, the transition metal ion in their ground state D or F being most common, do possess orbital angular momentum. For such ions, as Co^{2+} and Ni^{2+}, the magnetic moment is given by:

$$\mu_{(S+L)} = \sqrt{4S(S+1)+L(L+1)}$$

In which L represents the orbital angular momentum quantum number for the ion.

The spin magnetic moment is insensitive to the environment of metal ion, the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and thereby an orbital magnetic moment with reference to a given axis, it must be possible to transform the orbital into a fully equivalent orbital by rotation about that axis. For octahedral complexes the orbital angular momentum is absent for A_{1g}, A_{2g} and E_g term, but can be present for T_{1g} and T_{2g} terms. Magnetic moments of the complex ions with A_{2g} and E_g ground terms may depart from the spin-only value by a small amount. The magnetic moments of

the complexes possessing T ground terms usually differ from the high spin value and vary with temperature. The magnetic moments of the complexes having a $^6A_{1g}$ ground term are very close to the spin-only value and are independent of the temperature.

For octahedral and tetrahedral complexes in which spin-orbit coupling causes a split in the ground state an orbital moment contribution is expected. Even no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with higher states can appear due to spin-orbit coupling giving an orbital moment contribution.

Practically the magnetic moment value of the unknown complex is obtained on Gouy Magnetic balance. Faraday method can also be applied for the magnetic susceptibility measurement of small quantity of solid samples.

The gram susceptibility is measured by the following formula.

$$\chi_g = \frac{\Delta W}{W} \cdot \frac{W_{std}}{\Delta W_{std}} \cdot \chi_{std}$$

Where, χ_g = Gram Susceptibility

ΔW = Change in weight of the unknown sample with magnet on and off.

W = Weight of the known sample

ΔW_{std} = Change in weight of standard sample with magnets on and off.

W_{std} = Weight of standard sample.

χ_{std} = Gram susceptibility of the standard sample.

2.1.6 *CONDUCTIVITY*

The resistance of a sample of an electrolytic solution is defined by

$$R = \rho\ [l/A]$$

Where l is the length of a sample of electrolyte and A is the cross sectional area. The symbol ρ is the proportionality constant and is a property of a solution. This property is called resistivity or specific resistance. The reciprocal of resistivity is called conductivity, κ

$$\kappa = l/\rho = l/RA$$

Since l is in cm, A is in cm^2 and R in ohms (Ω), the units of κ are $\Omega^{-1}\ cm^{-1}$ or S cm^{-1} (Siemens per cm)

Molar Conductivity

If the conductivity κ is in $\Omega^{-1}\ cm^{-1}$ and the concentration C is in mol cm^{-3}, then the molar conductivity Λ is in $\Omega^{-1}\ cm^2\ mol^{-1}$ and is defined by

$$\Lambda = \kappa/C$$

Where C is the concentration of solute in mol cm^{-3}.

Conventionally solutions of 10^{-3} M concentration are used for the conductance measurement. Molar conductance values of different types of electrolytes in a few solvents are given below:

A 1: 1 electrolyte may have a value of 70-95 ohm^{-1} cm^2 mol^{-1} in nitromethane, 50-75 ohm^{-1} cm^2 mol^{-1} in dimethyl formamide and 100-160 ohm^{-1} cm^2 mol^{-1} in methyl cyanide. Similarly a solution of 2:1 electrolyte may have a value of 150-180 ohm^{-1} cm^2 mol^{-1} in nitromethane, 130-170 ohm^{-1} cm^2 mol^{-1} in dimethyl formamide and 140-220 ohm^{-1} cm^2 mol^{-1} in methyl cyanide[11,12,13].

2.1.7 *ELEMENTAL ANALYSES*

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligand as well as its metal complexes. Carbon, hydrogen and nitrogen analyses were carried out on a Perkin Elmer-2400 analyzer. Chloride was analyzed by conventional method[14]. For the metal estimation[15] a known amount of complex was decomposed with a mixture of nitric, perchloric and sulfuric acids in a beaker. It was then dissolved in water and made up to known volume so as to titrate it with standard EDTA. For chloride estimation, a known amount of the sample was decomposed in a platinum crucible and dissolved in water with a little concentrated nitric acid. The solution was then treated with

either silver nitrate or Barium chloride solution. The precipitate was then dried and weighed.

2.1.8 *THERMOGRAVIMETRIC ANALYSIS (T.G.A.)*

In a thermogravimetric analysis the mass of a complex in a controlled atmosphere is measured as its temperature is raised. When thermal dissociation occurs, the weight of any volatile ligand expelled is measured and the empirical formula of the product may usually be deduced. A plot of mass or mass percent as a function of time is called a thermogram, or a thermal decomposition curve[16,17]. In all the cases the samples were studied in the temperature range of 50-850 °C.

2.1.9 *JOB'S METHOD*

Job's method of continuous variation is a commonly used procedure for determining the composition of complexes in solution[18]. Job's method, as commonly practiced, is carried out in batch modes by mixing aliquots of two equimolar stock solutions of metal and ligand. These solutions are prepared in a manner such that the total analytical concentration of metal plus ligand is maintained constant while the ligand: metal ratio varies from flask to flask, that is:

$$C_M + C_L = k$$

Where C_M and C_L are the analytical concentrations of metal and ligand, respectively, and k is a constant. The absorbance is plotted as a function of mole fraction (X) of ligand or metal in the flasks.

$$\text{Where } X = X_L \text{ or } X_M$$

$$X_L = C_L/C_M + C_L$$

$$X_M = C_M/C_M + C_L$$

X_L is the mole fraction of the ligand and X_M is the mole fraction of the metal.

The resulting curves, called Job's plot, yields a maximum (or minimum) the position of which indicates the ligand: metal ratio of the complex in solution. For example, a maximum corresponding to 0.5 on the mole ratio fraction of ligand scale suggests a complex of 1:1 composition, while maxima at 0.67 and 0.75 indicate complexes of 2:1 and 3:1 ligand: metal ratios, respectively.

2.1.10 *MICROBIAL ASSAY*

The antibacterial activities were evaluated against different types of bacteria e.g., (*Escherchia coli, Staphylococus aureus* and *Cornybacterium diptheriae*) using paper disc diffusion method[19] in an agar medium. It appears that the compounds inhibit the growth of bacteria to a greater extent with increasing concentration. Potato dextrose media (PDA) rich in carbohydrates serve as the major nutrient source and is utilized by bacteria with the help of various

enzymes. These extracellular enzymes[20] secreted by these microorganisms diffuse out from the membrane of bacteria into the medium and lead to the breakdown of complex polysaccharides into the simpler monosaccharides. Though, the enzyme production is being affected, the little amount produced is sufficient to meet the need of the microorganisms to grow. The higher concentration proves fatal to the microorganisms, as the toxicity increases with the increasing concentration of the complexes. The test solutions were prepared in DMSO and soaked in filter paper of 5mm diameter. These discs were placed on the already seeded plates and incubated at 37 °C for 72 hours. During incubation the complex diffuses from the filter paper into the agar. The inhibition areas were observed after 72 hours. DMSO was used as a negative control and streptomycin as a standard drug.

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CHAPTER-III

SYNTHESIS AND PHYSICO-CHEMICAL STUDIES ON 14- AND 16- MEMBERED OCTAAZAMACROCYCLIC COMPLEXES DERIVED FROM HYDRAZINE WITH CO(II), NI(II), CU(II) AND ZN(II)

INTRODUCTION

Lindoy and co-workers[1-4] have made elegant studies on ligand design and metal recognition of polyaza and mixed polyazamacrocyclic complexes. A large number of macrocycles[5-16] and their complexes with transition metal ions have been synthesized and characterized. The chemistry of macrocyclic ligands has been extensively developed due to their mimicry to protein metal binding sites in biological systems[17] and metalloenzymes[18,19] and many more applications such as synthetic ionophores[20], as electrocatalysts in fuel cells[21], or as catalysts for decomposition of environmentally hazardous small molecules (NO_x, SO_x and CO_2)[22,23]. Continuing interest in these compounds has been reflected from their applications to ion selectivity[24,25] and use as radioimmunotherapeutic agents[26]. The macrocycles of different ring sizes are now readily achieved through conventional methods[20,27-33]. The pore size selectivity is also important[34,35] in the macrocycles. Several reports[7,36,37] have appeared concerning the chemistry of binuclear macrocyclic complexes, especially structural, magnetism correlation and bioinorganic modelling studies. Macrocyclic ligands play an important role in stabilizing the unusual oxidation states of metal ions and receptors for substrates of widely differing physical and chemical properties[3,38]. Several macrocyclic ligands derived from hydrazine

precursors have been reported[8,27,39,40] and most of these studies deal with mononuclear complexes. Reports[41,42] were published on the synthesis of macrocyclic complexes obtained from polyamines and formaldehyde. Various macrocyclic complexes have been synthesized by the template condensation of amines with aldehydes in the presence of metal ions, particularly formaldehyde has been utilized for the cyclization to link the amine moieties[43,44,45]. The metal template synthesis is found to direct the steric course of the condensation reaction towards ring closure[43,46,47]. A large number of macrocyclic complexes have been prepared[43,48] by template condensation reactions of primary diamines, formaldehyde and ammonia. Several reports appeared obtained for the synthesis of octaazamocrocycles[8,42]. Octaazamacrocycles exhibit interesting co-ordination properties in spite of the large cavity size formed by the macrocyclic backbone, capable of forming stable mono- and di-nuclear metal complexes, as well as stabilizing various anions in their protonated form[49,50]. Goedken and Peng have reported[42] the synthesis of 14-membered octaazamacrocyclic complexes by the template condensation reaction of butane-2,3-dione dihydrazone with formaldehyde. This chapter deals with the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) octaazamacrocyclic complexes, $[ML^1X_2]$ and $[ML^2X_2]$ (M = Co(II), Ni(II),

Cu(II) and Zn(II) and X = Cl or NO_3) by the template condensation reaction of hydrazine, formaldehyde and 1,2-dibromoethane or 1,3-dibromopropane.

EXPERIMENTAL

Materials and Methods

The metal salts $MX_2 \cdot nH_2O$ (M = Co and Ni; n = 6; X = Cl, NO_3), $MX_2 \cdot nH_2O$ (M = Cu; n = 3 and 2; X = NO_3 and Cl) and $ZnCl_2$, $Zn(NO_3)_2 \cdot 6H_2O$ (All Merck) were commercially available pure samples. Hydrazine hydrate (85%) (Sigma), 37% formaldehyde solution, 1,2-dibromoethane and 1,3-dibromopropane (All Merck) were used as received. Methanol used as a solvent was dried before use.

Synthesis of Dichloro/nitrato [1,2,4,5,8,9,11,12-octaazacyclotetradecane] metal(II) [ML^1X_2] (M = Co(II), Ni(II), Cu(II) and Zn(II); X = NO_3 or Cl).

A methanolic solution (~25 mL) of formaldehyde (0.02 moles) was added drop-wise to a methanolic solution (~25 mL) of hydrazine hydrate (0.04 moles). The mixture was stirred for several hours. Then a methanolic solution (~25 mL) of the metal salt (0.01 mole) was added followed by the addition of 1,2-dibromoethane (0.02 moles) leading to the formation of a solid product on stirring for six hours. The solid product thus formed was filtered, washed several times with methanol and dried in vacuo.

Synthesis of Dichloro/nitrato [1,2,4,5,8,9,10,12,13-octaazacyclohexadecane] metal(II), [ML^2X_2] (M = Co(II), Ni(II), Cu(II) and Zn(II); X = NO_3 or Cl).

The procedure was similar to the one mentioned above, except that 1,3-dibromopropane (0.02 moles) was used instead of 1,2-dibromoethane.

Physical Measurements

The elemental analyses was obtained by using a Perkin Elmer-2400 C,H,N analyzer. The IR spectra (4000-200 cm^{-1}) as KBr/CsI pellets were recorded on a Perkin Elmer-2400 spectrometer. ^1H FT-NMR spectra were recorded in DMSO-d_6 using a Jeol Eclipse 400 spectrometer. Magnetic Susceptibility measurements were carried out using a Faraday balance at 25 °C. Metals and chloride were determined volumetrically[51] and gravimetrically[52], respectively. Electronic spectra in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. EPR spectra were recorded on a JEOL JES RE2X EPR spectrometer at room temperature. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained on an APX 135 digital conductivity meter equilibrated at 25 ± 0.05 °C.

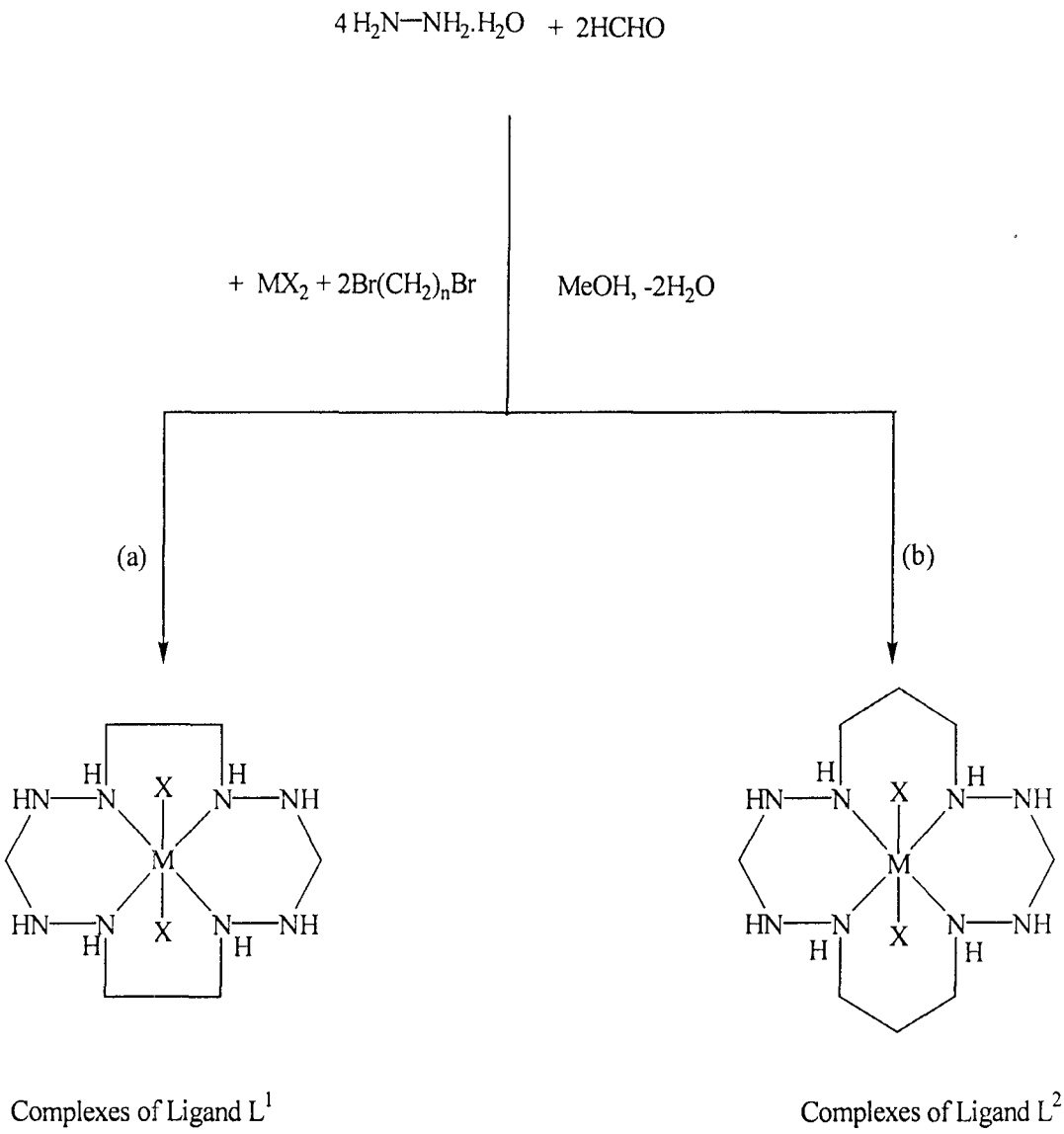
RESULTS AND DISCUSSION

A series of octaazamacrocyclic complexes, [ML^1X_2] and [ML^2X_2] (M = Co(II), Ni(II), Cu(II) and Zn(II); X = NO_3 or Cl) have been synthesized by the template condensation of hydrazine, formaldehyde

and 1,3-dibromopropane or 1,2-dibromoethane in 2:1:1 molar ratio as shown in Scheme 1. All complexes are stable to the atmosphere and are completely soluble in water and DMSO. The results of elemental analyses (Table-I) agree well with the proposed structures of the complexes. The low molar conductance values of all the compounds in DMSO at room temperature support[53] the non-ionic nature of these complexes. All attempts to grow single crystal suitable for X-ray crystallographic studies failed inspite of inordinate efforts.

IR SPECTRA

The prominent bands in the IR spectra of the complexes are shown in Table-II. The presence of a sharp single band in the 3210-3260 cm^{-1} region assignable[54] to coordinated N-H stretching mode of secondary amine and the absence of bands characteristics of the NH_2 groups of the hydrazine moiety in all the complexes indicate formation of a macrocyclic framework (Scheme 1). This was further corroborated by the appearance of a band around 1175 cm^{-1} characteristic of ν(C-N) and the presence of a medium intensity band in 410-450 cm^{-1} region which corresponds to the ν(M-N) vibration[55]. However, a band appearing around 940-980 cm^{-1} in all the complexes may be attributed[56] to N-N stretching mode. The coordination of the nitrate and chloro groups has been ascertained by bands occurred in the 230-240 and 270-300 cm^{-1}



Where, M = Co(II), Ni(II), Cu(II) and Zn(II), X = Cl or NO_3
n = 2 or 3

Scheme 1 Formation of the Complexes

Table I: Elemental analyses, color, yield, molar conductance, and melting point values of the compounds.

Compounds	F.W. (Calc.)	Color	Yield (%)	Found (calc.)%					Molar Conductance ($ohm^{-1}cm^2mol^{-1}$) /M.p. (°C)
				M	Cl	C	H	N	
$[CoL^1(NO_3)_2]$	387.21	Brown	60	15.0 (15.2)	-	18.5 (18.6)	5.1 (5.2)	36.0 (36.2)	20/ > 300
$[CoL^2(NO_3)_2]$	415.24	Brown	62	14.0 (14.2)	-	23.0 (23.1)	5.7 (5.8)	33.5 (33.7)	17/ > 300
$[CoL^1Cl_2]$	334.11	Dark brown	61	17.5 (17.6)	21.0 (21.2)	21.5 (21.6)	6.0 (6.0)	33.2 (33.5)	19/ > 300
$[CoL^2Cl_2]$	362.17	Brown	64	16.0 (16.3)	19.3 (19.5)	26.2 (26.5)	6.7 (6.7)	30.5 (30.9)	24/ > 300
$[NiL^1(NO_3)_2]$	387.00	Light purple	56	15.1 (15.2)	-	18.4 (18.6)	5.2 (5.6)	36.0 (36.2)	19/ > 300
$[NiL^2(NO_3)_2]$	415.02	Dark purple	50	14.0 (14.1)	-	22.8 (23.1)	5.6 (5.8)	33.4 (33.7)	17/ > 300
$[NiL^1Cl_2]$	333.87	Purple	54	17.5 (17.6)	21.0 (21.2)	21.5 (21.6)	6.0 (6.0)	33.4 (33.6)	21/ > 300
$[NiL^2Cl_2]$	361.92	Purple	59	16.0 (16.2)	19.5 (19.6)	26.3 (26.5)	6.5 (6.7)	30.8 (30.9)	22/ > 300
$[CuL^1(NO_3)_2]$	391.78	Green	55	16.0 (16.2)	-	18.3 (18.4)	5.1 (5.1)	35.5 (35.7)	14/ > 300

$[CuL^2(NO_3)_2]$	419.83	Dark green	58	15.0 (15.1)	-	22.7 (22.9)	5.8 (5.8)	33.1 (33.4)	18/ > 300
$[CuL^1Cl_2]$	338.68	Light green	58	18.5 (18.7)	20.9 (20.9)	21.0 (21.3)	5.9 (5.9)	33.0 (33.1)	15/ > 300
$[CuL^2Cl_2]$	366.73	Dark green	52	17.0 (17.3)	19.1 (19.3)	26.0 (26.2)	6.6 (6.6)	30.2 (30.5)	23/ > 300
$[ZnL^1(NO_3)_2]$	393.66	Colorless	66	18.0 (18.3)	-	35.2 (35.6)	5.1 (5.1)	35.2 (35.6)	18/ > 300
$[ZnL^2(NO_3)_2]$	421.71	Colorless	65	22.6 (22.8)	-	33.0 (33.2)	5.6 (5.7)	33.0 (33.2)	19/ > 300
$[ZnL^1Cl_2]$	340.56	Colorless	62	21.0 (21.2)	20.8 (20.6)	32.6 (32.9)	5.7 (5.9)	32.6 (32.9)	22/ > 300
$[ZnL^2Cl_2]$	368.61	Colorless	61	26.0 (26.1)	19.0 (19.2)	30.1 (30.4)	6.6 (6.6)	30.1 (30.4)	24/ > 300

Table II: IR vibrational frequencies (cm^{-1}) of compounds.

Compounds	v(N-H)	v(C-N)	v(M-N)	v(N-N)	v(M-O)	N(M-Cl)
$[CoL^1(NO_3)_2]$	3226	1184	417	952	232	-
$[CoL^2(NO_3)_2]$	3255	1180	423	960	237	-
$[CoL^1Cl_2]$	3248	1185	423	940	-	285
$[CoL^2Cl_2]$	3260	1178	420	943	-	280
$[NiL^1(NO_3)_2]$	3220	1175	417	973	237	-
$[NiL^2(NO_3)_2]$	3215	1170	442	974	238	-
$[NiL^1Cl_2]$	3210	1160	422	960	-	288
$[NiL^2Cl_2]$	3215	1172	428	966	-	300
$[CuL^1(NO_3)_2]$	3246	1180	410	949	240	-

$[CuL^2(NO_3)_2]$	3250	1182	424	954	230	-
$[CuL^1Cl_2]$	3230	1176	416	968	-	289
$[CuL^2Cl_2]$	3245	1180	421	972	-	292
$[ZnL^1(NO_3)_2]$	3212	1165	440	980	240	-
$[ZnL^2(NO_3)_2]$	3240	1164	432	950	237	-
$[ZnL^1Cl_2]$	3228	1182	437	950	-	270
$[ZnL^2Cl_2]$	3225	1595	450	972	-	280

regions which may reasonably be assigned [8,57] to ν(M-O) of the ONO_2 group and ν(M-Cl), respectively. Additional bands around ~1408, 1296 and 1026 in the spectra of nitrato complexes were obtained consistent with the monodentate coordination of the nitrato group.

Electronic Spectra and magnetic Data

The appearance of two bands appearing in the 14,000-14,450 and 21,000-21,350 cm^{-1} regions for the Co(II) complexes may reasonably be assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively (Table-III) consistent with the presence of an octahedral geometry around the cobalt(II) ion . The magnetic moment values of 4.50-4.60 B.M. range (Table-III) further support the electronic spectral data.

The electronic spectra of the Ni(II) complexes show two main bands in the 11,200-11,330 cm^{-1} and 17,150-17,450 cm^{-1} regions may reasonably be ascribed[58] to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively consistent with an octahedral geometry around the nickel(II) ion. Further confirmation regarding the octahedral environment around the Ni(II) ion has been obtained from the observed magnetic moments (Table-III).

The electronic spectra of the Cu(II) complexes show a main broad band in the region 19,000-19,400 cm^{-1} with a shoulder in the region

Table III: Magnetic moments(B.M.), electronic spectral bands (cm^{-1}) with their assignments and EPR spectral parameters for the complexes.

Compounds	μ_{eff} (B.M.)	Band position/cm^{-1}	Assignments	$g_{\parallel}$	$g_{\perp}$	G
$[CoL^1(NO_3)_2]$	4.58	14,000	$^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$(F)	–	–	–
		21,000	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$(P)			
$[CoL^2(NO_3)_2]$	4.60	14,100	$^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$(F)	–	–	–
		21,150	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$(P)			
$[CoL^1Cl_2]$	4.55	14,450	$^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$(F)	–	–	–
		21,350	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$(P)			
$[CoL^2Cl_2]$	4.50	14,350	$^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$(F)	–	–	–
		21,300	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$(P)			
$[NiL^1(NO_3)_2]$	3.12	11,250	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$(F)	–	–	–
		17,150	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$(P)			

$[NiL^2(NO_3)_2]$	3.15	11,200 17,200	$^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$(F) $^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$(P)	–	–	–
$[NiL^1Cl_2]$	3.12	11,300 17,400	$^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$(F) $^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$(P)	–	–	–
$[NiL^2Cl_2]$	3.10	11,330 17,450	$^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$(F) $^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$(P)	–	–	–
$[CuL^1(NO_3)_2]$	1.76	16,100 19,400	$^2B_{1g} \rightarrow ^2B_{2g}$ $^2B_{1g} \rightarrow ^2E_g$	2.20	2.10	2.0
$[CuL^2(NO_3)_2]$	1.78	16,150 19,250	$^2B_{1g} \rightarrow ^2B_{2g}$ $^2B_{1g} \rightarrow ^2E_g$	2.24	2.10	2.4
$[CuL^1Cl_2]$	1.73	16,450 19,000	$^2B_{1g} \rightarrow ^2B_{2g}$ $^2B_{1g} \rightarrow ^2E_g$	2.23	2.11	2.09
$[CuL^2Cl_2]$	1.70	16,300 19,200	$^2B_{1g} \rightarrow ^2B_{2g}$ $^2B_{1g} \rightarrow ^2E_g$	2.25	2.13	1.9

16,100-16,450 cm^{-1} may reasonably be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively characteristic of a distorted octahedral geometry around the copper(II) ion. The observed magnetic moments in the 1.70-1.78 B.M. range further support the proposed distortion of the octahedral geometry.

EPR Spectra

The room temperature EPR spectra of the Cu(II) macrocyclic complexes show a single broad band with $g_{\|}$ and $g_{\perp}$ values of 2.20-2.25 and 2.10-2.15, respectively, (Table-III). The $g_{\|} > g_{\perp} > 2.02$ implies[59] that $^2B_1$ is the ground state having the unpaired electron in the $d_{x^2-y^2}$ orbital. Proctor and co-workers have postulated[60] that the magnitude of the ratio $G = (g_{\|} -2)/(g_{\perp}-2)$ indicate the possibility of exchange interaction in the copper(II) complexes. The G values for the present complexes fall in the range 1.9-2.4, ($G < 4$) which indicates considerable exchange interaction in the solid complexes. All the copper complexes show considerable covalent character, as the $g_{\|}$ values are less than 2.3.

^{1}H NMR Spectra

The ^{1}H NMR data (Table-IV) for all mononuclear Zn(II) complexes, $[ZnL^1X_2]$ and $[ZnL^2X_2]$ show a multiplet in the region 6.86-6.94 ppm which arguably assigned to the secondary amino protons C-NH-N (4H) of the hydrazine moiety. A multiplet in the region 3.08-3.19 ppm

Table IV: ^1H NMR spectroscopic data of the compounds.

Compounds	C-NH-N	N-CH_2-N	C-CH_2-C	N-CH_2-C
$[ZnL^1(NO_3)_2]$	6.88	2.90	-	3.19
$[ZnL^2(NO_3)_2]$	6.90	2.95	1.80	3.14
$[ZnL^1Cl_2]$	6.86	2.92	-	3.08
$[ZnL^2Cl_2]$	6.94	2.93	1.90	3.15

in all the complexes correspond to the which corresponds to the methylene protons N-CH_2-C (8H) adjacent to the nitrogen atom of the amino moiety. Another multiplet appeared at 1.80 and 1.90 ppm for the complexes [ZnL^2Cl_2] and [$ZnL^2(NO_3)_2$], respectively may reasonably be assigned[61,62] to the middle methylene protons C-CH_2-C (4H) of the propane chain. A multiplet observed in the 2.90-2.95 ppm region may be attributed to the methylene protons N-CH_2-N (4H). None of the complexes were found to give any signal assignable to the primary amino protons indicating that the NH_2 group has condensed with formaldehyde and dibromoalkane.

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CHAPTER-IV

SYNTHESIS AND CHARACTERIZATION OF HEXAAZAMACROCYCLIC COMPLEXES WITH Co(II), Ni(II), Cu(II) AND Zn(II) DERIVED FROM PHTHALALDEHYDE AND 2,6- DIAMINOPYRIDINE.

INTRODUCTION

The chemistry of macrocyclic complexes has been a fascinating area of research interest to the chemists all over the world. The continued interest in designing new macrocyclic complexes is because of their use as models to study the magnetic exchange phenomena[1], NMR shift and relaxation probes of the dynamic solution conformation of molecules[2], as bioconjugates for monoclonal antibody radioisotope labelling[3]. Mergerum and his co-workers have reported[4,5] extensive investigations on the interaction of Cu^{2+} and Ni^{2+} with macrocycles containing nitrogen donor atoms. A large number of polyazamacrocyclic complexes have been reported[6-9] and a variety of research has been concerned with synthetic, kinetic and structural aspects of polyazamacrocyclic complexes. The synthetic studies of polyazamacrocycles add significance if the resulting complexes can be used as models for natural products[10], such as metalloporphyrins, vitamin B_{12} and chlorophyll. It is well established that the transition metal ion may act as template for the preparation of Schiff-base macrocyclic complexes[11] to direct the steric course of condensation reaction which ultimately ends with the ring closure[10,12]. The macrocycles of different ring sizes are now readily available by convenient methods[10,13,14]. A number of macrocyclic complexes have been prepared[15-17] by the template condensation of 2,6-diaminopyridine in the presence of

metal ions as templates. A number of macrocycles have been synthesized[18-20] through the condensation of aromatic dialdehydes and primary diamines in the presence of metal ions as templates. Colak and his co-workers have reported[21] macrocyclic imine oxime complexes prepared by the template condensation of o-phenylenediamine, phthalaldehyde, 2,6-diacetylpyridine in methanol medium. This chapter discusses the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) hexaazamacrocyclic complexes, $[MLX_2]$ [M = Co(II), Ni(II), Cu(II) and Zn(II) and (X = Cl or NO_3)] through the template condensation reaction of 2,6-diaminopyridine with o-phthalaldehyde.

EXPERIMENTAL

Materials and Methods

The metal salts $MX_2{\cdot}nH_2O$ (M = Co and Ni; n = 6; X = Cl, NO_3), $MX_2{\cdot}nH_2O$ (M = Cu; n = 3 and 2; X = NO_3 and Cl) and $ZnCl_2$, $Zn(NO_3)_2{\cdot}6H_2O$ (All Merck) were commercially available pure samples and were used as received. The chemicals o-phthalaldehyde (Fluka) and 2,6-diaminopyridine (Merck) were used as received. Analytical grade methanol was used as a solvent.

Synthesis of Dichloro/nitrato [3,5:12,14 dipyridyl 8,9:17,18dibenzo-2,4,6,11,13,14-hexacyclooctadecane-1,6,10,15-tetraene]metal(II), $[MLX_2]$ (M = Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or NO_3).

To a stirred methanolic solution (~20ml) of metal salt (0.01mole) taken in a two necked round bottomed flask was added the methanolic solution (~25ml) of o-phthalaldehyde (0.02 moles) followed by the drop-wise addition of 2,6-diaminopyridine (0.02moles) with continuous stirring and gentle heating (~40°C) for about 3-4 hours. This afforded the isolation of solid product which was filtered, washed several times with methanol and dried in vacuo.

Measurements

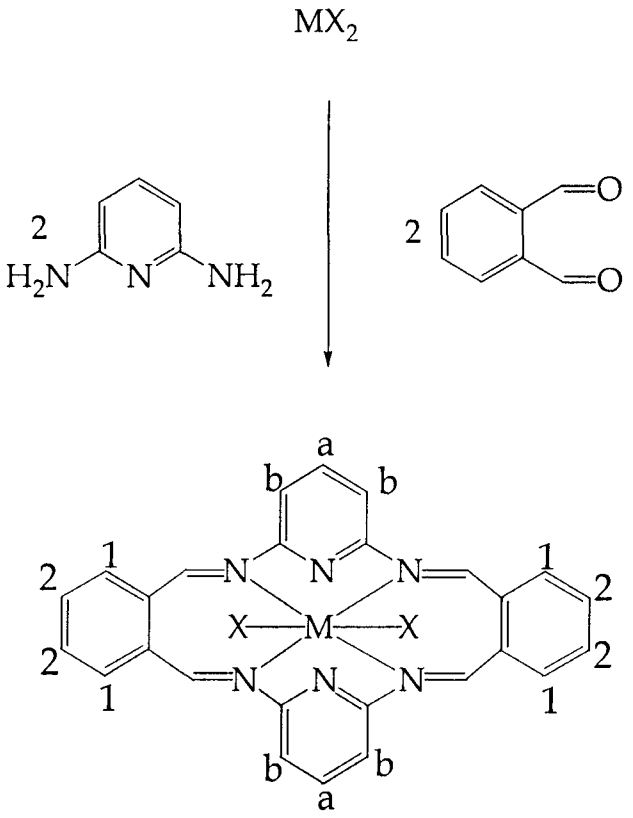
The elemental analyses data were obtained by using a Heracus Carlo Erba 1108 C,H,N analyzer. The FTIR spectra were recorded as CsCl discs using a Perkin Elmer-2400 spectrophotometer over the range 200-4000 cm^{-1}. Proton NMR spectra in DMSO-d_6 were recorded using a Bruker DRX 300 NMR spectrophotometer with TMS as internal standard. UV-Visible spectra of the compounds in DMSO were collected on a Pye-Unicam 8800 spectrophotometer. EPR spectra were obtained on a JEOL JES RE2X EPR spectrometer. Metals and chloride were determined volumetrically[22] and gravimetrically[23], respectively. Magnetic susceptibility measurements were carried out using a Faraday balance at 25 °C. The electrical conductivities of 10^{-3} M solutions in DMSO were performed on an APX 135 Digital conductivity meter equilibrated at 25 ± 0.05 °C.

RESULTS AND DISCUSSION

A novel series of mononuclear hexaazamacrocyclic complexes [MLX_2] [M = Co(II), Ni(II), Cu(II) and Zn(II), X = Cl or NO_3] were synthesized by the template condensation reactions of o-phthalaldehyde with 2,6-diaminopyridine in methanol in 2:2 molar ratio (Scheme 1). All complexes are stable to atmosphere. The complexes were found soluble in DMSO, DMF and THF. Elemental analyses data (Table-I) are consistent with the proposed stoichiometry of the complexes. The low molar conductance values measured in DMSO (10^{-3}M) are suggestive[24] of the non-electrolytic nature of these complexes.

IR Spectra

The main bands and their assignments are listed in (Table-II). The IR spectra of all the complexes do not show bands corresponding to amino or carbonyl groups, instead a strong intensity band appeared in the region 1595-1615cm^{-1} that may be assigned[25] to coordinated ν(C=N), alongwith the characteristic ring vibrations of pyridine moiety, appearing in the regions, 401-410, 601-610 and 1575-1585 cm^{-1} assignable[26] to 16b (out-of-plane ring deformation) and 6a and 8a (in-plane ring deformation) mode respectively. The phenyl ring vibrations were observed at their estimated positions. A sharp intensity band in the region, 430-455cm^{-1} corresponds[27] to ν(M–N) vibration. However,



M = Co(II), Ni(II), Cu(II) and Zn(II), X = Cl or NO_3

Scheme 1 Formation of hexaazamacrocyclic complexes

Table I: Elemental analyses, color, yield, molar conductance and melting point values of the compounds.

Compounds	F.W. (Calc.)	Color	Yield (%)	Found (Calc.) %					Molar Conductivity/ M.p. $ohm^{-1}\ cm^{-2}\ mol^{-1}$/(°C)
				M	Cl	C	H	N	
[Co L $(NO_3)_2$]	597.41	Brown	58	9.85 (9.86)	-	52.25 (52.27)	3.04 (3.04)	18.75 (18.76)	20 / 210
[Co LCl_2]	544.31	Brown	60	10.83 (10.83)	13.00 (13.03)	57.35 (57.37)	3.31 (3.33)	15.42 (15.44)	16 / 220
[NiL$(NO_3)_2$]	597.16	Brownish green	60	9.80 (9.83)	-	52.27 (52.29)	3.04 (3.04)	18.75 (18.76)	18 / 245
[Ni L Cl_2]	544.06	Dark Green	63	10.75 (10.78)	13.01 (13.03)	57.37 (57.39)	3.33 (3.33)	15.42 (15.45)	22 / 230
[CuL$(NO_3)_2$]	601.97	Blackish brown	58	10.52 (10.55)	-	51.85 (51.87)	3.01 (3.01)	18.6 (18.6)	24 / 225
[CuLCl_2]	548.87	Brown	61	11.55 (11.57)	12.90 (12.92)	56.85 (56.89)	3.30 (3.30)	15.30 (15.31)	20 / 235
[ZnL$(NO_3)_2$]	603.85	Brown	62	10.81 (10.82)	-	51.70 (51.71)	3.00 (3.00)	18.51 (18.55)	19 / 215
[ZnLCl_2]	570.75	Dark brown	66	11.42 (11.45)	12.40 (12.42)	54.70 (54.71)	3.17 (3.17)	14.70 (17.72)	16 / 200

Table II: IR vibrational frequencies (cm^{-1}) of complexes.

Compounds	ν(C=N)	ν(M-N)	ν(M-O)	ν(M-Cl)	Pyridine Ring Vibrations		
					16b	6a	8a
$[CoL(NO_3)_2]$	1605	430	230	280	410	605	1575
$[CoLCl_2]$	1600	435	235	290	405	601	1578
$[NiL(NO_3)_2]$	1595	455	225	285	407	604	1580
$[NiLCl_2]$	1610	445	220	270	405	607	1577
$[CuL(NO_3)_2]$	1615	430	240	265	403	610	1583
$[CuLCl_2]$	1595	440	230	260	401	606	1579
$[ZnL(NO_3)_2]$	1605	450	220	255	407	609	1582
$[ZnLCl_2]$	1615	445	275	275	402	604	1585

the coordination of the nitrate and chloro groups have been confirmed by the bands in the 220–240 and 260–290cm^{-1} regions, which may be assigned[25] to ν(M–O) of the ONO_2 group and ν(M–Cl), respectively. Additional bands around ~1410, 1230 and 1015 cm^{-1} in the spectra of nitrato complexes were obtained characteristic of the monodentate coordination of the nitrato group[27].

Electronic Spectra and Magnetic Data

The electronic spectra of Co(II) complexes showed two main bands in the 14,500–14,550 and 22,900–23,100 cm^{-1} regions, which may be attributed to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively (Table-III). The positions of these bands were found to be consistent with the octahedral geometry around the cobalt(II) ion[28]. The observed magnetic moment values (Table-III) complement the electronic spectral data.

The complexes derived from Ni(II) ion exhibit two bands in 11,000–11,150 and 17,800–17,900cm^{-1} region assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively suggesting an octahedral geometry around Nickel(II) ion[28]. The further evidence regarding the confirmation of octahedral environment around Ni(II) ion has been obtained from the observed values of magnetic moment (Table-III).

Table III: Magnetic moments, electronic spectral bands (cm^{-1}) with their assignments and EPR spectral parameters for the complexes.

Compounds	μ_{eff}(B.M.)	Band Position (cm^{-1})	Assignments	EPR		
				$g_{\|}$	$g_{\perp}$	G
$[CoL(NO_3)_2]$	4.73	14,500	$^4T_{1g}$ (F) → $^4A_{2g}$(F)	–	–	–
		22,900	$^4T_{1g}$ (F) → $^4T_{1g}$ (P)			
$[CoLCl_2]$	4.69	14,550	$^4T_{1g}$ (F) → $^4A_{2g}$ (F)	–	–	–
		23,100	$^4T_{1g}$ (F) → $^4T_{1g}$ (P)			
$[NiL(NO_3)_2]$	3.17	11,000	$^3A_{2g}$(F) → $^3T_{1g}$(F)	–	–	–
		17,800	$^3A_{2g}$(F) → $^3T_{1g}$(P)			
$[NiLCl_2]$	3.20	11,150	$^3A_{2g}$(F) → $^3T_{1g}$(F)	–	–	–
		17,900	$^3A_{2g}$(F) → $^3T_{1g}$(P)			
$[CuL(NO_3)_2]$	1.75	19,250	$^2B_{1g}$ → ^2E_g	2.16	2.08	2.00
		16,400	$^2B_{1g}$ →$^2B_{2g}$			
$[CuLCl_2]$	1.78	19,150	$^2B_{1g}$ → ^2E_g	2.21	2.11	1.91
		16,150	$^2B_{1g}$ →$^2B_{2g}$			

However, a broad band in the region, 19,150–19,250cm^{-1} has been recorded along with a shoulder in the region, 16,150–16,400cm^{-1} in the electronic spectra of Cu(II) complexes which may reasonably be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transition, respectively, characteristic of a distorted octahedral geometry around thee copper(II) ion[28]. The magnetic moment values of 1.75 and 1.78 B.M. further support the electronic spectral data.

EPR Spectra

The EPR spectra of the Cu(II) complexes recorded at room temperature and their $g_{\|}$ and $g_{\perp}$ values have been calculated. Both the complexes gave a single broad signal with calculated $g_{\|}$ and $g_{\perp}$ values as 2.16 and 2.08 for $[CuL(NO_3)_2]$ and 2.21 and 2.11 for $[CuLCl_2]$ indicative[29] of the presence of unpaired electron in the $d_{x^2-y^2}$ orbital suggesting that $^2B_1$ is the ground state. In view of the fact that the $g_{\|}$ values are less than 2.3 there appears to be a considerable covalent character[30]. In addition to it the calculated G = $(g_{\|} - 2) / (g_{\perp} - 2)$ less than 4 indicate a considerable exchange interaction between the Cu^{2+} ions in these complexes.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of $[ZnL(NO_3)_2]$ shows a singlet at 8.08 ppm corresponding[31] to the four equivalent imine protons CH=N(4H). The spectrum shows a triplet (δ_H 8.05) and a doublet (δ_H 7.73) assigned[32] to

the para (H_a) and meta pyridyl (H_b) protons, respectively. However, a doublet and a triplet observed[32] at δ 6.89 and δ7.26 may be assigned for H_1 and H_2 phenyl protons, respectively. The ^1H NMR spectrum of $[ZnL(NO_3)_2]$ does not show any bands assignable to the uncondensed moieties which further support the macrocyclic framework (Scheme 1).

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CHAPTER-V

METAL ION-DIRECTED SYNTHESIS OF 16-MEMBERED TETRAAZAMACROCYCLIC COMPLEXES AND THEIR PHYSICO-CHEMICAL STUDIES

INTRODUCTION

There has been considerable interest in structural, thermodynamic and kinetic studies of the metal complexes with polyazamacrocycles because of their significant implications in analytical, biological and medicinal applications[1-5]. Structural factors such as the cavity size, type and number of donor atoms and stereochemical rigidity have been shown to play significant roles in determining the binding features of macrocycles towards metal ions[6,7]. It is well established that the transition metal ions may act as templates for the preparation of schiff base macrocyclic complexes which serve to direct the steric course of the reaction preferentially towards cyclic rather than oligomeric or polymeric products[8]. Various macrocycles have been synthesized[9-11] through template condensation involving *o*-phenylenediamine as a sub-unit in the macrocyclic framework in view of the fact that both aliphatic and aromatic diamines are valuable building blocks for the preparation of macrocyclic diamides[12], polyamides[13] and azacrowns[14]. Certain polyamide macrocycles[15] mimic naturally occurring macrocyclic ionophores with their ability to transport metal cations across biological and artificial membranes. Macrocycles especially the ones containing aromatic moieties are known to form charge transfer complexes with a variety of guests. These macrocycles were used to study complexation

of diverse guests to provide new insights into noncovalent binding interactions, chiefly cation π-interactions which involve the stabilization of a positive charge by the face of an aromatic ring[16]. Macrocyclic polyamines continue to be of great interest in coordination chemistry. The importance of these compounds is due to their role played as polyprotic bases, multidentate ligands and important biological substances[17,18]. They also form well-defined complexes with a wide range of metal ions. A number of macrocycles have been synthesized[19-21] by the condensation of aromatic dialdehydes and primary diamines in the presence of metal ions as templates.

In view of the fact that macrocycles bearing polyaromatic rings provide a class of noncovalent intermolecular forces leading to multiple applications[1-5], it was thought worthwhile to synthesize and characterize a series of 16-membered tetraazamacrocyclic complexes composed entirely of aromatic rings formed by the template condensation of *o*-phenylenediamine and *o*-phthalaldehyde in presence of Co(II), Ni(II), Cu(II) and Zn(II). This chapter deals with the synthesis and physico-chemical studies on tetraimine macrocyclic complexes.

EXPERIMENTAL

Materials and Methods

The metal salts, $MX_2.nH_2O$ (M = Co and Ni; n = 6; X = NO_3, Cl), $MX_2.nH_2O$ (M = Cu; n = 3 and 2; X = NO_3 and Cl) and $ZnCl_2$, $Zn(NO_3)_2.6H_2O$ (All Merck), were commercially available pure samples. The chemicals *o*-phthalaldehyde (Fluka) and *o*-phenylenediamine (Reachim) were used as received. Analytical grade ethanol and methanol were used as solvents.

Synthesis of Dichloro/nitrato bis(*o*-phenylenediamine) metal(II) (A).

o-phenylenediamine (20 mmol) dissolved in EtOH solution (50 cm^3) of was added dropwise to a MeOH solution (15 cm^3) of $MX_2.nH_2O$ (M = Co and Ni; n = 6; X = NO_3, Cl), $MX_2.nH_2O$ (M = Cu; n = 3 and 2; X = NO_3 and Cl) and $ZnCl_2$, $Zn(NO_3)_2.6H_2O$ and the mixture was stirred for 1 hour. The resulting complex thus formed was isolated, washed several times with MeOH and dried in vacuo.

Synthesis of Dichloro/nitrato [3,4;7,8;11,12;15,16-tetrabenzo-2,5,10,13-tetraazacyclohexadecane-1,5,9,13-tetraene] metal(II), [MLX_2] [M = Co(II), Ni(II), Cu(II) and Zn(II); X = Cl or NO_3]

A solution of (A) (10 mmol) in MeOH (50 cm^3) was added to a solution of *o*-phthalaldehyde (20 mmol) in MeOH (15 cm^3), and the

mixture was stirred for 2-3 hours. The volume was then reduced to 10 cm^3 by rotary-evaporation. The precipitated complex was filtered off, washed several times with methanol and dried in vacuo (Scheme-1).

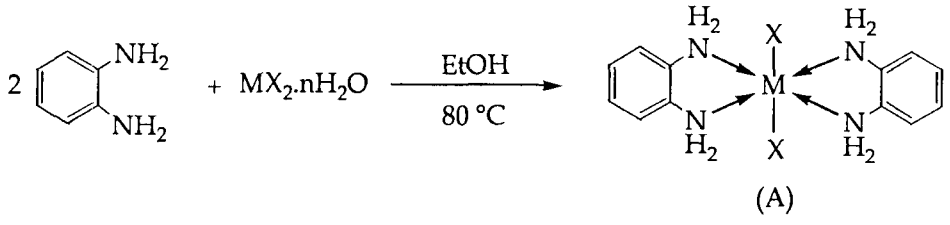
Ligand (L):

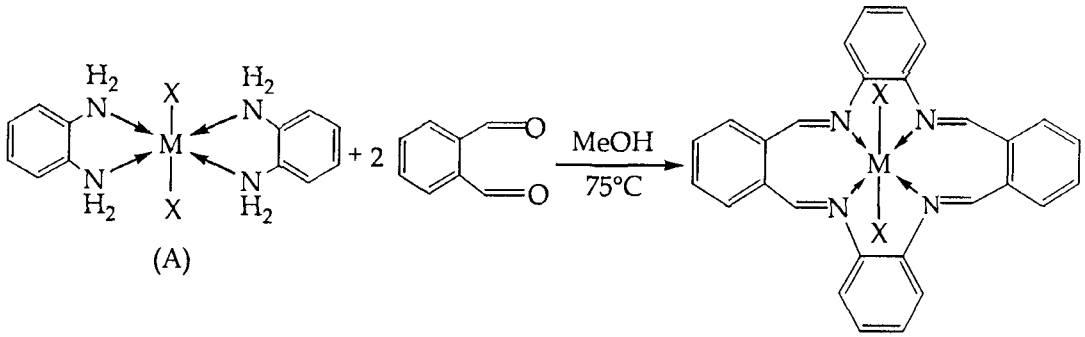
[3,4;7,8;11,12;15,16-tetrabenzo-2,5,10,13-tetraazacyclohexadecane-1,5,9,13-tetraene]

The macrocyclic ligand was prepared by demetallating the macrocyclic complex[17] in an acidic medium (Scheme 2).

Physical Measurements

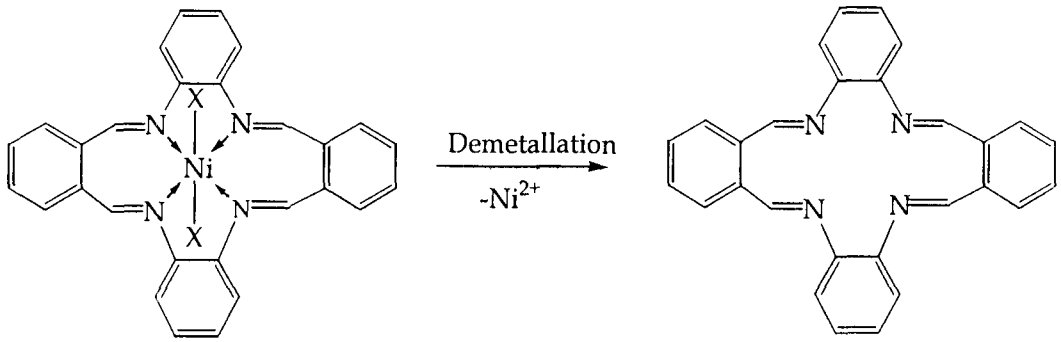
The carbon, hydrogen and nitrogen analyses were carried out on a Perkin Elmer-2400 C,H,N analyzer. Infrared spectra were recorded on a Perkin Elmer-2400 Spectrophotometer with KBr/CsI pellets, electronic absorption spectra was recorded on a Pye-Unicam model 8800, UV/Vis Spectrophotometer. Proton FT-NMR spectra in DMSO-d_6 were recorded on a Jeol Eclipse 400 Spectrometer with TMS as internal standard. Metals and chlorides were determined volumetrically[22] and gravimetrically[23], respectively. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained on a Digital conductivity meter APX 135 equilibrated at 25 ± 0.05 °C. Magnetic susceptibility was measured at room temperature on a Faraday balance. Spectroscopic measurement





Where M = Co(II), Ni(II), Cu(II) and Zn(II), X = Cl or NO_3

Scheme 1 Suggested structure for 16-membered tetraazamacrocyclic complexes



Scheme 2 Preparation and proposed structure of the ligand

(Job's method) was performed at room temperature on an Elico SL 159 UV-VIS spectrophotometer. Thermoanalyses of the complexes were performed on model METTLER TOLEDO STAR^e SW 7.01. In all the cases 50-850 °C range was studied. The biological screening of the complexes was carried out using disc diffusion method.

Results and Discussion

Dichloro/nitrato bis(*o*-phenylenediamine) metal(II) (A), was reacted with *o*-phthalaldehyde (1:2 molar ratio) in MeOH solution, resulting macrocyclic complexes of the type, $[MLX_2]$. The level of purity of the compounds was checked by T.L.C. on Silica Gel coated plates. The complexes were dissolved in DMSO using ethylacetate (85%), methanol (10%) and acetic acid (5%) as eluent. Only one spot was observed in each case after developing in an iodine chamber, indicating that the compounds were pure. The formation of the macrocyclic framework encapsulating metal ion has been deduced from the appearance of new bands viz., ν(C=N), ν(M-N), ν(M-Cl) or ν(M-ONO_2) characteristic of coordinated imine nitrogen, chloride and nitrate moieties. The involvement of chloride and nitrate coordinated to metal has been further confirmed by thermal analyses data. The proposed stoichiometry $[M(C_{28}H_{20}N_4)X_2]$ of the complexes corresponds to the results of elemental analyses (Table-I). Job's method[24] of continuous

Table I: Analytical data, color, melting point, yield and molar conductance of the complexes.

Compounds	F.W. (Calc.)	Color	M.p. (°C)	Yield (%)	Found (Calc.)%					Molar Conductance ($cm^2\Omega^{-1}mol^{-1}$)
					M	Cl	C	H	N	
L	412.49	Yellow	200	50	-	-	81.00 (81.53)	4.89 (4.89)	13.00 (13.58)	-
[Co L $(NO_3)_2$]	595.43	Olive green	215	60	9.82 (9.90)	-	56.44 (56.48)	3.37 (3.39)	14.06 (14.11)	20
[Co LCl_2]	542.33	Olive green	220	65	10.81 (10.87)	13.02 (13.07)	62.05 (62.01)	3.71 (3.71)	10.29 (10.33)	22
[NiL$(NO_3)_2$]	595.19	Brown	245	63	9.82 (9.86)	-	56.47 (56.50)	3.36 (3.38)	14.09 (14.12)	23
[Ni L Cl_2]	542.09	Light brown	230	67	10.78 (10.83)	13.02 (13.08)	62.00 (62.04)	3.72 (3.72)	10.30 (10.33)	19
[CuL$(NO_3)_2$]	600.04	Dark green	250	70	10.53 (10.59)	-	56.00 (56.05)	3.32 (3.36)	14.00 (14.01)	17
[CuLCl_2]	546.95	Light green	243	72	11.57 (11.62)	12.93 (12.97)	61.44 (61.49)	3.66 (3.69)	10.18 (10.24)	24
[ZnL$(NO_3)_2$]	601.88	Dark orange	218	65	10.80 (10.86)	-	55.84 (55.88)	3.35 (3.35)	13.92 (13.96)	25
[ZnLCl_2]	548.78	Orange	210	69	11.87 (11.91)	12.85 (12.92)	61.25 (61.28)	3.66 (3.67)	10.14 (10.20)	27

variation was used to determine the composition of the complexes in solution which gave the data suggesting 1:1 metal to ligand ratio of the complexes. The non-electrolytic nature of the complexes was based on the molar conductivity data. The magnetic moment data and the bands observed in their electronic spectra have been used to assign the geometry of the complexes. All the complexes, in general, are non-hygroscopic, stable solids, insoluble in water with varying solubility in common organic solvents. Single crystals of the compounds could not be isolated even after inordinate efforts suitable for x-ray studies.

IR Spectra

The characteristic bands observed in the IR Spectra (4000-200 cm^{-1}) provide information regarding the formation of macrocyclic framework in the complexes and were compared with bands appeared in dichloro/nitrato bis(*o*-phenylenediamine) metal(II) (A). The positions of the most relevant bands and their assignments for the ligand and complexes are mentioned in Table-II. The absence of bands around ~3400 and 1650 cm^{-1} characteristic of νNH_2 and δNH_2 respectively of free primary diamine and the absence of band expected to appear ~1700 cm^{-1} for free aldehydic moiety suggest condensation between amino group and aldehydic group has taken place. Further evidence regarding condensation has been obtained by appearance of a new strong

Table II: IR Spectral data of the macrocyclic ligand and its complexes.

Compounds	ν(C=N)	ν(M–N)	ν(M–O)	ν(M–Cl)	Phenyl Ring vibrations		
L	1620	-	-	-	1465	1064	805
$[CoL(NO_3)_2]$	1592	450	235	-	1440	1080	805
$[CoLCl_2]$	1600	440	-	305	1452	1085	792
$[NiL(NO_3)_2]$	1590	450	240	-	1480	1100	790
$[NiLCl_2]$	1585	442	-	290	1470	1090	747
$[CuL(NO_3)_2]$	1595	445	230	-	1467	1074	752
$[CuLCl_2]$	1600	448	-	300	1475	1080	790
$[ZnL^1(NO_3)_2]$	1592	446	240	-	1480	1100	800
$[ZnL^1Cl_2]$	1595	440	-	295	1440	1080	775

intensity band in the region 1585-1620 cm^{-1} which may be assigned to ν(C=N)[25]. However a negative shift of 20-30 cm^{-1} in ν(C=N) stretching band in all macrocyclic complexes suggest that imine nitrogens involve in coordination to metal ions. This is further corroborated by the appearance of a medium intensity band in the region 450-440 cm^{-1} assignable to ν(M-N) vibration. While the bands appearing in the region 1480-1440, 1100-1064 and 805-740 cm^{-1} correspond to phenyl ring vibrations. The bands observed in the complexes at 240-230 and 305-290 cm^{-1} regions may unambiguously be assigned to the ν(M-O) of the ONO_2 group and ν(M-Cl), respectively. The additional bands observed around 1410, 1300 and 1020 cm^{-1} are consistent with the monodentate coordination mode of the nitrato group[26].

Electronic Spectra

The electronic spectra of the Cobalt(II) macrocyclic complexes, $[CoL(NO_3)_2]$ and $[CoLCl_2]$ exhibit three bands in the 8,772-8,880; 18,500-18,739 and 20,000-20,746 cm^{-1} regions, which correspond to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively (Table-III), consistent with the octahedral geometry around the cobalt(II) ion[27]. The magnetic moment values 4.60 and 4.75 B.M. (Table-III) further support the electronic spectral data.

Table III: Magnetic moments (B.M.) and electronic spectral data (cm^{-1}) for the macrocyclic complexes.

Compounds	μ_{eff} (B.M)	Band position (cm^{-1})	Assignments
$[CoL(NO_3)_2]$	4.60	8,772	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F)
		18,500	$^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F)
		20,746	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P)
$[CoLCl_2]$	4.75	8,880	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F)
		18,739	$^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F)
		20,000	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P)
$NiL(NO_3)_2]$	3.10	8,500	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F)
		13,698	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (P)
		27,027	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (F)
$[NiLCl_2]$	3.15	9,000	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F)
		13,448	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (P)
		27,230	$^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (F)
$[CuL(NO_3)_2]$	2.00	12,450	$^2B_{1g} \rightarrow {}^2A_{1g}$
		17,000	$^2B_{1g} \rightarrow {}^2E_g$
$[CuLCl_2]$	1.90	13,000	$^2B_{1g} \rightarrow {}^2A_{1g}$
		16,666	$^2B_{1g} \rightarrow {}^2E_g$

The octahedral geometry around the Nickel(II) ion has been assigned due to appearance of three bands in 8,500-9,000; 13,448-13,698 and 27,027-27,230 cm^{-1} regions assignable[27] to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively. The observed magnetic moments (Table-III) suggest the formation of high-spin octahedral complexes of Ni(II) ion and thus confirm the electronic spectral findings.

The electronic spectra of tetragonally distorted octahedral Copper(II) complexes usually show three bands viz., $^2B_{1g} \rightarrow {}^2A_{1g}$; $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ in the increasing order of their energies. It has been observed that the energy level sequence depends on the amount of distortion due to ligand field and Jahn-Teller effect[28]. The electronic spectra of the Cu(II) complexes show two characteristic bands in the range 12,450-13,000 and 16,666-17,000 cm^{-1} characteristic for $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. However the band expected ca 16200 cm^{-1} for $^2B_{1g} \rightarrow {}^2B_{2g}$ transition could not be observed due to low intensity. Copper(II) complexes show magnetic moment values 1.90 and 2.00 B.M. further corroborate a distorted octahedral structure.

^{1}H NMR Spectra

The signal arising from CH=N protons (4H) of $[ZnLCl_2]$ appears at (δ8.05), reasonably suggest[29] that the condensation between primary

amine and a carbonyl group has taken place and thus confirm the formation of the proposed macrocyclic framework (Scheme 1). The spectrum shows four multiplets at (δ6.89, δ7.20, δ7.31 and δ7.50) characteristic of protons of the benzenoid rings. However, these proton resonance signals have been found to be slightly upfield shifted in the macrocyclic ligand derived from demetallation reaction.

Job's Plot

Job's method of continuous variation is a commonly used procedure for determining the composition of complexes in solution. The solutions of metal salts and ligand were prepared in a manner such that the total analytical concentration of metal plus ligand is maintained constant while the ligand : metal ratio varies from flask to flask, that is:

$$C_M + C_L = k$$

Where C_M and C_L are the analytical concentrations of metal and ligand, respectively, and k is a constant. The absorbance is plotted as a function of mole fraction (X) of ligand or metal in the flasks. The resulting curve is known as Job's plot.

$$\text{Where, } X = X_L \text{ or } X_M$$

$$X_L = C_L / C_M + C_L$$

X_L= Mole fraction of ligand.

X_M = Mole fraction of metal.

The job diagrams (Figure 3 and Figure 4) obtained for the copper and cobalt complexes at λ = 600 and 500 nm respectively, consists of two straight lines intersecting at X = 0.5, thus suggest a complex of 1:1 composition. The same profiles were observed when the diagrams were constructed at different wavelengths.

Thermogravimetric Analyses

The thermogravimetric studies made on Ni(II) and Cu(II) macrocyclic complexes are mentioned below:

The TGA curves (Figure 5 and Figure 6) obtained in N_2 atmosphere over the temperature range 50-850 °C show that the Ni(II) complex is more stable than Cu(II) complex. The Ni(II) complex was stable upto 310 °C and its decomposition started at this temperature, while as in Cu(II) complex it was stable upto 230 °C. None of the complexes contain hydrated or lattice water molecules. The first step in the decomposition of both the complexes corresponds to the removal of the coordinated chloride or nitrate ions in Ni(II) and Cu(II) complexes. With rising temperature, the complexes begin to decompose and the final residue found was NiO and CuO. The total loss of weight agree with the corresponding calculated data.

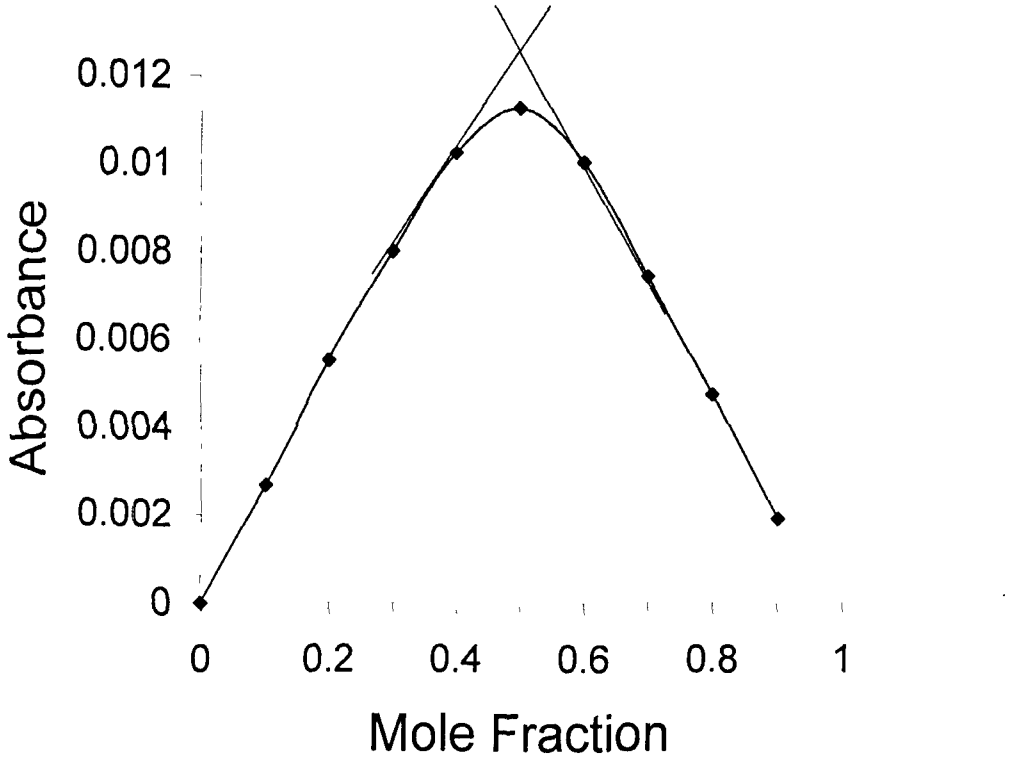


Figure 3 Job's plot (600nm) obtained for Cu(II) complex

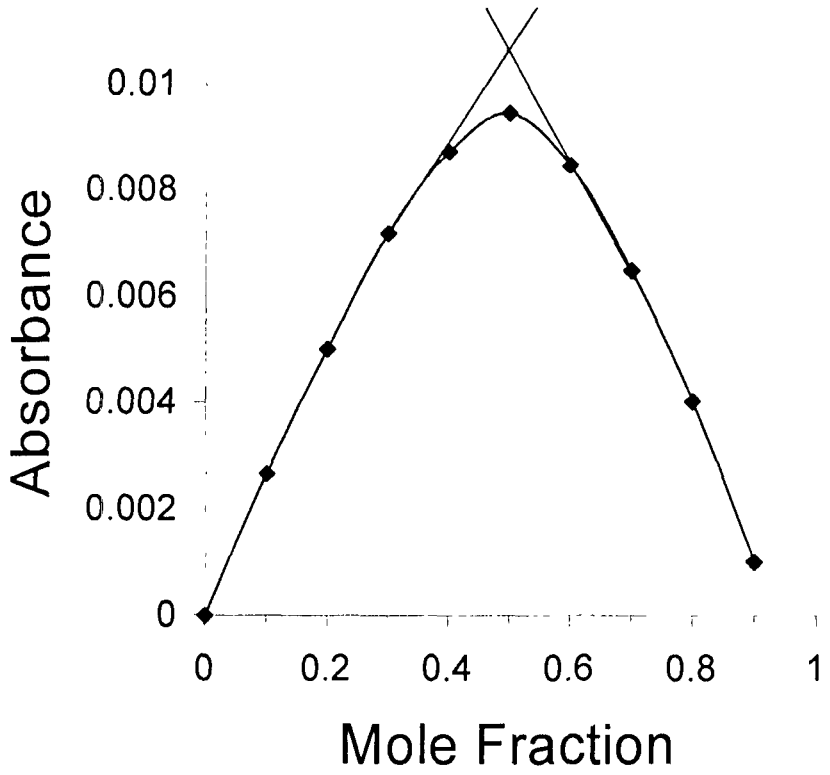


Figure 4 Job's plot (500nm) obtained for Co(II) complex

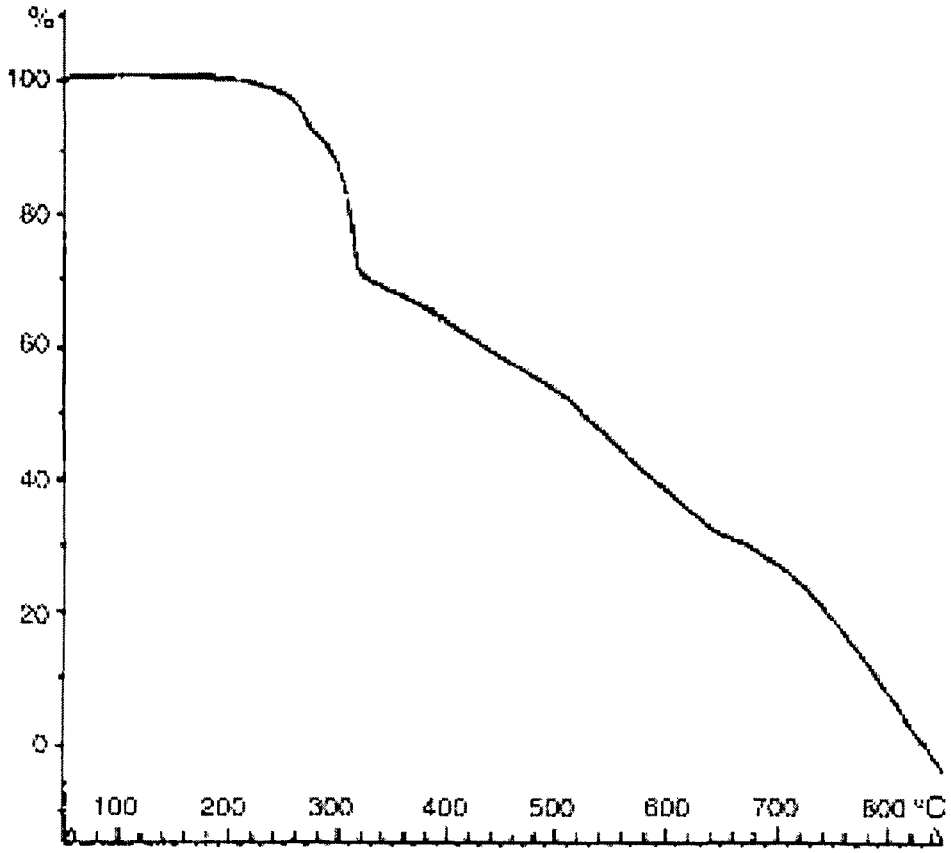


Figure 5 TGA curve for Ni(II) complex

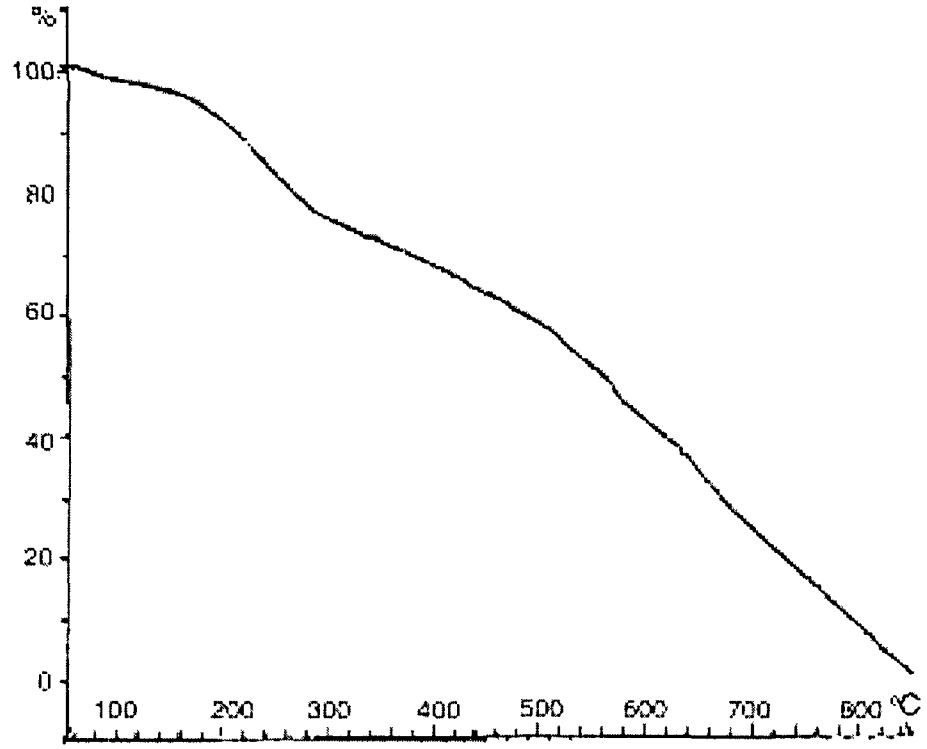


Figure 6 TGA curve for Cu(II) complex

Antimicrobial Screening:

The antibacterial activity[30] of complexes of Co(II), Ni(II), Cu(II) and Zn(II) against *Escherchia coli, Staphylococcus aureus and Cornybacterium diptheriae* was carried out by paper disc diffusion method. In this method, 0.1mL of inoculum of the test organism was spread uniformly on the surface of the agar medium in a Petri plate by using a spreader. The 150-ppm solutions of the complexes were prepared, respectively, by dissolving 15 mg of complex in 100mL of DMSO. The whatmann filter paper discs of 5mm diameter were soaked in the solutions. After drying it was placed on nutrient agar plates. The plates were incubated at 37 °C. During incubation, the complex diffuses from the filter paper into the agar. The inhibition areas were observed after 72 hours. DMSO was used as a negative control and Streptomycin as a standard drug. The result of these studies is shown in Figure 7. The results reveal that all the complexes are active against these microorganisms.

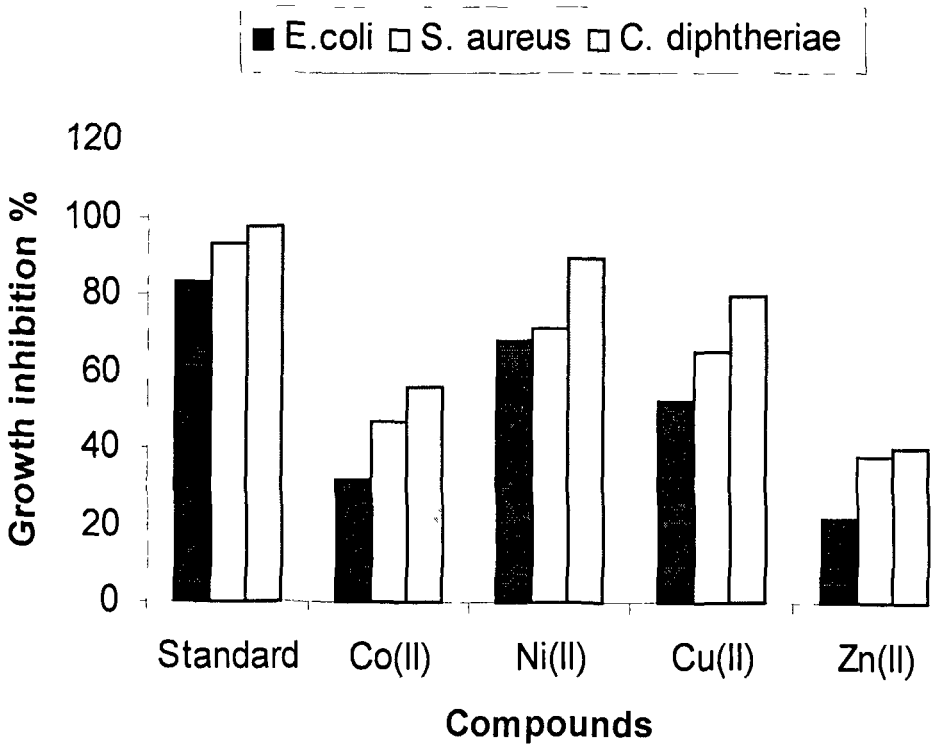


Figure 7 Antibacterial activity for the macrocyclic complexes

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